

=> file reg  
FILE 'REGISTRY'  
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FILE 'REGISTRY'

	E GLYCOLIDE/CN
L1	1 S E3
	E LACTIDE/CN
L2	1 S E3
	E DIETHYLBENZENE/CN
L3	1 S E3
	E 1,2-DIETHYLBENZENE/CN
L4	1 S E3
	E 1,3-DIETHYLBENZENE/CN
L5	1 S E3
	E 1,4-DIETHYLBENZENE/CN
L6	1 S E3
	E DODECANE/CN
L7	1 S E3
	E DECANE/CN
L8	1 S E3
	E OCTYLBENZENE/CN
L9	1 S E3
	E PROPYLBENZENE/CN
L10	1 S E3
	E ETHYLBENZENE/CN
L11	1 S E3

FILE 'HCA'

L12	4128 S L1 OR GLYCOLIDE#
L13	8081 S L2 OR LACTIDE#
L14	3319 S L3 OR L4 OR L5 OR L6 OR DIETHYLBENZENE# OR DIETHYL#(A)B
L15	14899 S L7 OR DODECANE# OR C12H26
L16	23807 S L8 OR DECANE# OR C10H22
L17	780 S L9 OR OCTYLBENZENE# OR OCTYL#(A)BENZENE#
L18	5966 S L10 OR PROPYLBENZENE# OR (PROPYL# OR PR) (A)BENZENE#
L19	29238 S L11 OR ETHYLBENZENE# OR (ETHYL# OR ET) (A)BENZENE#
L20	23172 S AZEOTROP? OR COAZEOTROP?
L21	360945 S DISTILL? OR DIST# OR DISTN# OR CODISTILL? OR CODIST# OR
L22	2 S L12 AND (L14 OR L15 OR L16 OR L17 OR L18 OR L19)
L23	1 S L22 AND (L20 OR L21)

L24 9 S L13 AND (L14 OR L15 OR L16 OR L17 OR L18 OR L19)  
L25 1 S L24 AND (L20 OR L21)  
L26 73084 S LACTONE# OR (CYCLIC? OR CYCLIZ? OR CYCLIS?) (2A)ESTER#  
L27 657 S L26 AND (L14 OR L15 OR L16 OR L17 OR L18 OR L19)  
L28 22 S L27 AND L20  
L29 164 S L27 AND L21  
L30 18 S L28 AND L29  
L31 2675 S DILACTONE#  
L32 15 S L31 AND (L14 OR L15 OR L16 OR L17 OR L18 OR L19)  
L33 5 S L32 AND (L20 OR L21)  
L34 14 S L22 OR L23 OR L24 OR L25 OR L33  
L35 20 S (L28 OR L30) NOT L34

=> file hca

FILE 'HCA'

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=> d l34 1-14 cbib abs hitstr hitind

L34 ANSWER 1 OF 14 HCA COPYRIGHT 2005 ACS on STN

137:324277 **Azeotropic distillation** of cyclic esters

of hydroxy organic acids. Cockrem, Michael Charles Milner; Kovacs, Istvan (USA). U.S. Pat. Appl. Publ. US 2002157937 A1 20021031, 15 pp. (English). CODEN: USXXCO. APPLICATION: US 2001-809534 20010315.

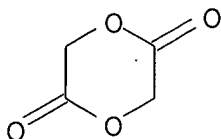
AB Cyclic esters of hydroxy org. acids can be produced and recovered via **azeotropic distn.** In certain embodiments cyclic esters, such as **glycolide** and **lactide**, can be produced from a fermn. broth or other feed stream that comprises a hydroxy org. acid, an NH<sub>4</sub><sup>+</sup> salt of a hydroxy org. acid, an amide of a hydroxy org. acid, or an ester of a hydroxy org. acid using **azeotropic distn.** The hydroxy org. acid of the feed stream or the hydroxy org. acid derived from the feed stream by decompn. is reacted to produce the cyclic ester. In other embodiments a crude compn. of a cyclic ester of an org. ester can be purified using **azeotropic distn.**

IT 502-97-6P, Glycolide

(azeotropic distn. of cyclic esters of hydroxy org. acids)

RN 502-97-6 HCA

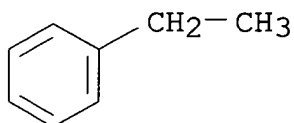
CN 1,4-Dioxane-2,5-dione (9CI) (CA INDEX NAME)



IT 100-41-4, Ethylbenzene, uses 103-65-1,  
 Propylbenzene 112-40-3, n-Dodecane  
 124-18-5, Decane 2189-60-8,  
 Octylbenzene 25340-17-4, Diethylbenzene  
 (azeotropic distn. of cyclic esters of  
 hydroxy org. acids)

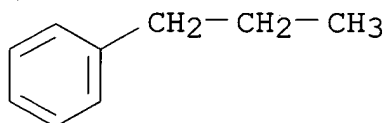
RN 100-41-4 HCA

CN Benzene, ethyl- (7CI, 8CI, 9CI) (CA INDEX NAME)



RN 103-65-1 HCA

CN Benzene, propyl- (8CI, 9CI) (CA INDEX NAME)



RN 112-40-3 HCA

CN Dodecane (8CI, 9CI) (CA INDEX NAME)

Me- (CH<sub>2</sub>)<sub>10</sub>-Me

RN 124-18-5 HCA

CN Decane (8CI, 9CI) (CA INDEX NAME)

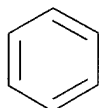
Me- (CH<sub>2</sub>)<sub>8</sub>-Me

RN 2189-60-8 HCA

CN Benzene, octyl- (9CI) (CA INDEX NAME)

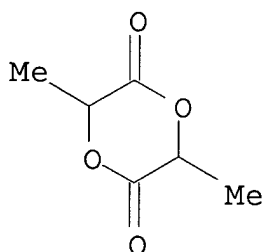
Me- (CH<sub>2</sub>)<sub>7</sub>-Ph

RN 25340-17-4 HCA  
CN Benzene, diethyl- (8CI, 9CI) (CA INDEX NAME)



2 ( D1-Et )

IT 95-96-5, Lactide  
(azeotropic distn. of cyclic esters of  
hydroxy org. acids)  
RN 95-96-5 HCA  
CN 1,4-Dioxane-2,5-dione, 3,6-dimethyl- (9CI) (CA INDEX NAME)



IC ICM B01D003-38  
ICS C07C051-46; C07C059-06; C07C069-68  
NCL 203014000  
CC 16-1 (Fermentation and Bioindustrial Chemistry)  
ST azeotropic distn cyclic ester hydroxy org acid;  
lactide glycolide azeotropic  
distn  
IT Fermentation  
(azeotropic distn. of cyclic esters of  
hydroxy org. acids produced in)  
IT Distillation  
(azeotropic; azeotropic distn. of  
cyclic esters of hydroxy org. acids)  
IT 502-97-6P, Glycolide 4511-42-6P, L-  
Lactide  
(azeotropic distn. of cyclic esters of  
hydroxy org. acids)  
IT 50-21-5, Lactic acid, reactions 50-21-5D, Lactic acid,  
1,2-dodecanediol ester 79-33-4, L-Lactic acid, reactions

- 1119-87-5D, 1,2-Dodecanediol, ester with lactic acid  
(azeotropic distn. of cyclic esters of hydroxy org. acids)
- IT 100-41-4, Ethylbenzene, uses 103-65-1, Propylbenzene 112-40-3, n-Dodecane 124-18-5, Decane 1330-20-7, Xylene, uses 2189-60-8, Octylbenzene 25340-17-4, Diethylbenzene  
(azeotropic distn. of cyclic esters of hydroxy org. acids)
- IT 95-96-5, Lactide  
(azeotropic distn. of cyclic esters of hydroxy org. acids)
- L34 ANSWER 2 OF 14 HCA COPYRIGHT 2005 ACS on STN
- 137:170334 Biodegradable **lactide**-based (co)polymers, their preparation, and their polyisocyanate-crosslinked polymers. Shirahama, Hiroyuki; Yasuda, Hajime; Baba, Eiichi (Japan Science and Technology Corporation, Japan). Jpn. Kokai Tokkyo Koho JP 2002234934 A2 20020823, 11 pp. (Japanese). CODEN: JKXXAF. APPLICATION: JP 2001-34940 20010213.
- AB Biodegradable copolymers are prep'd. by ring-opening polymn. of **lactides** with .epsilon.-caprolactone bearing .gtoreq.1 reactive substituents selected from OH, amino, or CO<sub>2</sub>H. Prepn. of biodegradable polymers by ring-opening polymn. of the .epsilon.-caprolactone is also claimed. Prepn. of biodegradable polymers by ring-opening polymn. of **lactides** with depsipeptides bearing phenolic OH which may be subsequently crosslinked with polyisocyanates. These reactive substituents and phenolic OH may have been protected before the polymn. then deprotected after the polymn. to make the polymers biodegradable. Thus, 4-benzoyloxycaprolactone (4BOCL) was copolymd. with L-**lactide** (L-LA) to give a 36:64 L-LA-4BOCL copolymer in yield 83.1%, Mn 5.7 .times. 10<sup>4</sup>, Mw/Mn 1.72, Tg -3.4', and Tm 159.6.degree.. The copolymer in THF was treated under H atm. in presence of Pt catalyst supported on activated C to convert Bz group to OH to give a deprotected copolymer showing excellent biodegradability in seawater.
- IC ICM C08G063-08  
ICS C08G063-91
- CC 37-3 (Plastics Manufacture and Processing)
- ST hydroxy caprolactone polymer prep'n biodegradable; amino caprolactone polymer prep'n biodegradable; carboxyl caprolactone polymer prep'n biodegradable; **lactide** reactive substituent caprolactone copolymer biodegradable; depsipeptide **lactide** copolymer prep'n biodegradable plastic; aliph polyester biodegradability prep'n deprotection crosslinking; polyisocyanate crosslinked depsipeptide **lactide** copolymer biodegradable

- IT Polyesters, preparation  
(aliph., isocyanate-crosslinked; prepn. of biodegradable homopolymers and copolymers of **lactides** and substituted .epsilon.-caprolactone and their crosslinked products)
- IT Polyesters, preparation  
(aliph.; prepn. of biodegradable homopolymers and copolymers of **lactides** and substituted .epsilon.-caprolactone and their crosslinked products)
- IT Polymers, preparation  
(biodegradable; prepn. of biodegradable homopolymers and copolymers of **lactides** and substituted .epsilon.-caprolactone and their crosslinked products)
- IT 447407-44-5P  
(crosslinked, biodegradable; prepn. of biodegradable homopolymers and copolymers of **lactides** and substituted .epsilon.-caprolactone and their crosslinked products)
- IT 563-76-8P, D,L-2-Bromopropionyl bromide 2987-06-6P,  
4-Benzyloxycyclohexanone 16652-64-5P, o-Benzyl-L-tyrosine  
22428-87-1P, 8-Hydroxy-1,4-dioxaspiro[4.5]**decane**  
92829-83-9P, 8-Benzyloxy-1,4-dioxaspiro[4.5]**decane**  
(intermediate in monomer prepn.; prepn. of biodegradable homopolymers and copolymers of **lactides** and substituted .epsilon.-caprolactone and their crosslinked products)
- IT 60-18-4, L-Tyrosine, reactions 100-39-0, Benzyl bromide  
(monomer prepn. from; prepn. of biodegradable homopolymers and copolymers of **lactides** and substituted .epsilon.-caprolactone and their crosslinked products)
- IT 168208-62-6P 447407-41-2P  
(monomer; prepn. of biodegradable homopolymers and copolymers of **lactides** and substituted .epsilon.-caprolactone and their crosslinked products)
- IT 447407-43-4P  
(prepn. and cyclization of; prepn. of biodegradable homopolymers and copolymers of **lactides** and substituted .epsilon.-caprolactone and their crosslinked products)
- IT 447407-40-1P  
(prepn. and deprotection of; prepn. of biodegradable homopolymers and copolymers of **lactides** and substituted .epsilon.-caprolactone and their crosslinked products)
- IT 65408-67-5P, .epsilon.-Caprolactone-L-**lactide** copolymer  
286432-61-9P 447407-42-3DP, hydrolyzed  
(prepn. of biodegradable homopolymers and copolymers of **lactides** and substituted .epsilon.-caprolactone and their crosslinked products)
- IT 447407-42-3P  
(prepn. of biodegradable homopolymers and copolymers of **lactides** and substituted .epsilon.-caprolactone and their crosslinked products)

IT 268728-43-4P 447407-40-1DP, hydrolyzed  
(prepn. of biodegradable homopolymers and copolymers of  
**lactides** and substituted .epsilon.-caprolactone and their  
crosslinked products)

IT 4746-97-8, 1,4-Cyclohexanedione monoethylene ketal  
(redn. of, monomer prep. from; prep. of biodegradable  
homopolymers and copolymers of **lactides** and substituted  
.epsilon.-caprolactone and their crosslinked products)

L34 ANSWER 3 OF 14 HCA COPYRIGHT 2005 ACS on STN

133:125176 Poly(D,L-lactide) nanocapsules prepared by a  
solvent displacement process: influence of the composition on  
physicochemical and structural properties. Mosqueira, Vanessa Carla  
Furtado; Legrand, Philippe; Pinto-Alphandary, Huguette; Puisieux,  
Francis; Barratt, Gillian (Departamento de Farmacia-Escola de  
Farmacia, Universidade Federal de Ouro Preto, Minas Gerais,  
35400000, Brazil). Journal of Pharmaceutical Sciences, 89(5),  
614-626 (English) 2000. CODEN: JPMSAE. ISSN: 0022-3549.  
Publisher: Wiley-Liss, Inc..

AB Nanocapsules (NC) were prep. by interfacial deposition of preformed  
biodegradable polymer (PLA50) after a solvent displacement process.  
The influence of the compn. used for the prep. of NC was evaluated  
in terms of particle size, polydispersity, zeta potential,  
homogeneity, and structural characteristics of the systems. The  
nature of the oil phase, polymer mol. wt., type and concn. of  
different surfactants were investigated to optimize the formulation  
to obtain NC suitable for i.v. administration. The influence of the  
physicochem. properties of the different oils used in NC prep. on  
the NC size was evaluated. The interfacial tension between the oil  
and water phases seems to have a greater effect on NC size than the  
oil viscosity. Miglyol 810 and Et oleate lead to the formation of  
smaller NC, probably because of the reduced interfacial tension.  
The polymer mol. wt. plays only a small role in NC surface charge in  
the presence of lecithin, whereas NC surface charge, size,  
polydispersity, and short-term stability were highly influenced by  
lecithin purity. It appears that the absence of Poloxamer 188 leads  
to smaller polydispersity, less contamination with nanospheres, and  
reduced formation of structures other than NC. Furthermore,  
electron microscopy and d. gradient d. techniques were used to  
examine the structure of the particles formed and their homogeneity.  
NC formation was evidenced by the bands with intermediate d. between  
nanoemulsion and nanospheres; however, other bands of low intensity  
were obsd. The presence of liposomes and multilayers in NC prep.  
was confirmed by electron microscopy. The percentage of  
carboxyfluorescein entrapped in different NC formulations allowed us  
to est. the contamination by liposomes. It has been show that,  
under our exptl. conditions, an excess of lecithin is an essential  
prerequisite for a stable prep. of PLA NC.

IT **112-40-3, Dodecane**  
 (polylactide nanocapsules prepd. by solvent displacement process)  
 RN 112-40-3 HCA  
 CN Dodecane (8CI, 9CI) (CA INDEX NAME)

Me- (CH<sub>2</sub>)<sub>10</sub>-Me

CC 63-6 (Pharmaceuticals)  
 Section cross-reference(s): 38  
 IT 111-62-6, Ethyl oleate **112-40-3, Dodecane**  
 1338-43-8, Span 80 18194-24-6, Dimyristoylphosphatidylcholine  
 18656-38-7, Dimyristoylphosphatidylcholine 26023-30-3,  
 Poly[oxy(1-methyl-2-oxo-1,2-ethanediyl)] 26680-10-4, Poly(D,L-  
**lactide**) 77466-09-2, Miglyol 840 97708-73-1, Miglyol 829  
 106392-12-5, Poloxamer 188 135945-29-8, Phospholipon 90  
 (polylactide nanocapsules prepd. by solvent displacement process)

L34 ANSWER 4 OF 14 HCA COPYRIGHT 2005 ACS on STN

130:173393 Interfacial and emulsion stabilizing properties of  
 amphiphilic water-soluble poly(ethylene glycol)-poly(lactic acid)  
 copolymers for the fabrication of biocompatible nanoparticles.  
 Gref, R.; Babak, V.; Bouillot, P.; Lukina, I.; Bodorev, M.;  
 Dellacherie, E. (BP 451, Laboratoire de Chimie Physique  
 Macromoleculaire, ENSIC, Nancy, 54001, Fr.). Colloids and Surfaces,  
 A: Physicochemical and Engineering Aspects, 143(2-3), 413-420  
 (English) 1998. CODEN: CPEAEH. ISSN: 0927-7757. Publisher:  
 Elsevier Science B.V..

AB The steric stabilization of microscopic **decane**-H<sub>2</sub>O-  
**decane** films (with a diam. of .apprx.100 .mu.m) and  
**decane**-in-H<sub>2</sub>O nanoemulsions (with mean droplet size of  
 .apprx.200 nm) by the adsorption layers of biocompatible and  
 biodegradable H<sub>2</sub>O-sol. surface-active poly(ethylene  
 glycol)-poly(lactic acid) (PEG-PLA) diblock copolymers with  
 different HLB was studied as a function of both PEG and PLA mol.  
 wts. (MW), varying from 0.5 to 10 kg/mol. In the MW range studied,  
 the stability or the lifetime of the microscopic emulsion films  
 (MEF) and of the nanoemulsions depends mainly on the length (lPLA)  
 of the hydrophobic PLA blocks (it increases with increase of lPLA),  
 and is characterized by a stepwise dependence on the surfactant  
 concn. A sharp transition, from very stable to unstable MEF and  
 emulsions, occurred at a well-defined crit. surfactant concn. C\*.  
 The PLA blocks, insol. in both **decane** and H<sub>2</sub>O, adopt the  
 most energetically favorable side-on orientation at the  
**decane**-H<sub>2</sub>O interface, whereas the PEG blocks are oriented  
 towards the H<sub>2</sub>O phase in a mushroom or brush conformation. The  
 length of the PLA blocks det. the minimal area per adsorbed  
 surfactant mol. at the interface and consequently the crit. concn.



C\*.

CC 66-2 (Surface Chemistry and Colloids)

Section cross-reference(s): 6, 36

ST emulsion film stabilizing ethyleneglycol **lactide** block copolymer; nanoemulsion stabilizing ethyleneglycol **lactide** block copolymer

L34 ANSWER 5 OF 14 HCA COPYRIGHT 2005 ACS on STN

130:154078 Manufacture of high optical-purity **lactide** by depolymerization using vaporized organic solvents at a lower temperature and higher pressure than conventional methods. Ohkaito, Makoto; Okuyama, Hisashi; Kawamoto, Tatsushi; Ohara, Hitomi (Shimadzu Corp., Japan). Jpn. Kokai Tokkyo Koho JP 11035579 A2 19990209 Heisei, 5 pp. (Japanese). CODEN: JKXXAF. APPLICATION: JP 1997-192108 19970717.

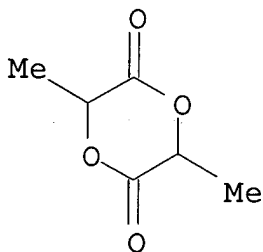
AB **Lactide** (I) is manufd. by depolymn. of lactic acid oligomer (II) with supplying vaporized org. solvents to the reaction system. I is useful as a material for biodegradable poly(lactic acid). L-II (Mw 1500, optical purity 98.0%) was depolymd. in the presence of Sn octylate at 160.degree. and 2.1 .times. 103 Pa for 2 h with introducing vaporized MePh to the reactor to give discoloration-free L-I (optical purity 97.7%).

IT 95-96-5P, **Lactide**

(manuf. of high optical-purity **lactide** by depolymn. using vaporized org. solvents under mild conditions)

RN 95-96-5 HCA

CN 1,4-Dioxane-2,5-dione, 3,6-dimethyl- (9CI) (CA INDEX NAME)

IT 124-18-5, **Decane**

(manuf. of high optical-purity **lactide** by depolymn. using vaporized org. solvents under mild conditions)

RN 124-18-5 HCA

CN Decane (8CI, 9CI) (CA INDEX NAME)

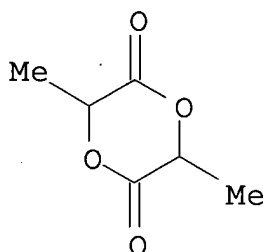
Me- (CH<sub>2</sub>)<sub>8</sub>-Me

IC ICM C07D319-12

- CC 35-2 (Chemistry of Synthetic High Polymers)  
Section cross-reference(s): 28
- ST **lactide** manuf polylactic acid depolymn toluene;  
biodegradable polylactic acid material **lactide** manuf;  
vaporized org solvent depolymn polylactic acid
- IT Polyesters, preparation  
(aliph., oligomeric; manuf. of high optical-purity  
**lactide** by depolymn. using vaporized org. solvents under  
mild conditions)
- IT Polymers, preparation  
(biodegradable, material for; manuf. of high optical-purity  
**lactide** by depolymn. using vaporized org. solvents under  
mild conditions)
- IT Depolymerization  
(manuf. of high optical-purity **lactide** by depolymn.  
using vaporized org. solvents under mild conditions)
- IT Solvents  
(org.; manuf. of high optical-purity **lactide** by  
depolymn. using vaporized org. solvents under mild conditions)
- IT **95-96-5P, Lactide** 4511-42-6P, **L-Lactide**  
(manuf. of high optical-purity **lactide** by depolymn.  
using vaporized org. solvents under mild conditions)
- IT 108-88-3, Toluene, uses **124-18-5, Decane**  
(manuf. of high optical-purity **lactide** by depolymn.  
using vaporized org. solvents under mild conditions)
- IT 26161-42-2P, Poly(L-lactic acid), sru 26811-96-1P, Poly(L-lactic  
acid)  
(oligomeric; manuf. of high optical-purity **lactide** by  
depolymn. using vaporized org. solvents under mild conditions)
- IT 26023-30-3, Poly(lactic acid), sru 26100-51-6, Poly(lactic acid)  
(oligomeric; manuf. of high optical-purity **lactide** by  
depolymn. using vaporized org. solvents under mild conditions)
- L34 ANSWER 6 OF 14 HCA COPYRIGHT 2005 ACS on STN
- 125:127644 Method for obtaining improved image contrast in migration  
imaging members. Limburg, William W.; Mammino, Joseph; Liebermann,  
George; Griffiths, Clifford H.; Shahin, Michael M.; Malhotra, Shadi  
L.; Chen, Liqin; Perron, Marie-Eve (Xerox Corp., USA). U.S. US  
5514505 A 19960507, 147 pp. (English). CODEN: USXXAM.  
APPLICATION: US 1995-441360 19950515.
- AB Disclosed is a process which comprises (a) providing a migration  
imaging member comprising (1) a substrate and (2) a softenable layer  
comprising a softenable material and a photosensitive migration  
marking material present in the softenable layer as a monolayer of  
particles situated at or near the surface of the softenable layer  
spaced from the substrate, (b) uniformly charging the imaging  
member, (c) imagewise exposing the charged imaging member to  
activating radiation at a wavelength to which the migration marking

material is sensitive, (d) causing the softenable material to soften and enabling a first portion of the migration marking material to migrate through the softenable material toward the substrate in an imagewise pattern while a second portion of the migration marking material remains substantially unmigrated within the softenable layer, and (e) contacting the second portion of the migration marking material with a transparentizing agent which transparentizes the migration marking material.

IT 95-96-5, 3,6-Dimethyl-1,4-dioxane-2,5-dione  
(transparentizing agent for electrophotog. migration imaging members)  
RN 95-96-5 HCA  
CN 1,4-Dioxane-2,5-dione, 3,6-dimethyl- (9CI) (CA INDEX NAME)



IC ICM G03G017-10  
NCL 430041000  
CC 74-3 (Radiation Chemistry, Photochemistry, and Photographic and Other Reprographic Processes)  
IT 50-44-2, 6-Mercaptopurine 50-89-5, Thymidine, uses 51-17-2, Benzimidazole 51-35-4, 4-Hydroxyproline 51-45-6, Histamine, uses 54-16-0, 5-Hydroxyindole-3-acetic acid, uses 54-77-3 54-95-5, 1,5-Pentamethylenetetrazole 55-22-1, Isonicotinic acid, uses 56-05-3, 2-Amino-4,6-dichloropyrimidine 56-06-4, 2,4-Diamino-6-hydroxypyrimidine 56-09-7, 4,6-Dihydroxy-2-aminopyrimidine 56-10-0 56-34-8, Tetraethyl ammonium chloride 56-93-9, Benzyl trimethyl ammonium chloride 57-71-6, 2,3-Butane dione monoxime 58-33-3, Promethazine hydrochloride 58-55-9, Theophylline, uses 58-56-0, Pyridoxine hydrochloride 58-61-7, Adenosine, uses 58-63-9, Inosine 58-96-8, Uridine 59-31-4, 2-Hydroxyquinoline 59-49-4, 2(3H)-Benzoxazolone 59-66-5 59-97-2, 2-Benzyl-2-imidazoline hydrochloride 60-27-5, Creatinine 61-12-1, Dibucaine hydrochloride 61-25-6, Papaverine hydrochloride 61-82-5, 3-Amino-1,2,4-triazole 63-45-6, Primaquine diphosphate 64-20-0, Tetramethyl ammonium bromide 65-19-0, Yohimbine hydrochloride 65-22-5, Pyridoxal hydrochloride 65-71-4, 2,4-Dihydroxy-5-methylpyrimidine 66-22-8, 2,4(1H,3H)-Pyrimidinedione, uses 66-71-7, 1,10-Phenanthroline 67-03-8, Thiamine hydrochloride 67-51-6, 3,5-Dimethylpyrazole 67-52-7,

Barbituric acid 67-71-0 68-05-3, Tetraethyl ammonium iodide 68-41-7, Cycloserine 68-94-0 69-09-0, Chlorpromazine hydrochloride 69-74-9, Cytosine arabinoside hydrochloride 69-89-6, Xanthine 71-91-0, Tetraethyl ammonium bromide 72-14-0 72-40-2, 4-Amino-5-imidazole carboxamide hydrochloride 73-24-5, 6-Aminopurine, uses 73-40-5, Guanine 75-57-0, Tetramethyl ammonium chloride 75-58-1, Tetramethyl ammonium iodide 76-29-9, 3-Bromocamphor 77-71-4, 5,5-Dimethylhydantoin 77-73-6, Dicyclopentadiene 78-19-3 78-40-0, Triethoxyphosphine oxide 78-51-3 79-92-5, Camphene 82-82-6, Pyridoxic acid 83-33-0, 1-Indanone 84-88-8, 8-Hydroxyquinoline-5-sulfonic acid 86-95-3, 2,4-Quinolinediol 87-39-8, Violuric acid 87-51-4, Indole-3-acetic acid, uses 87-90-1 89-00-9, 2,3-Pyridine dicarboxylic acid 89-01-0, 2,3-Pyrazine dicarboxylic acid 91-19-0, Quinoxaline 91-22-5, Quinoline, uses 91-44-1, 7-Diethylamino-4-methylcoumarin 91-56-5, Indole-2,3-dione 91-63-4, Quinaldine 92-48-8, 6-Methylcoumarin 92-53-5, 4-Phenylmorpholine 93-10-7, 2-Quinolinecarboxylic acid 93-37-8, 2,7-Dimethylquinoline 94-66-6, 2-Allylcyclohexanone 94-67-7, Salicylaldoxime 95-11-4, 5-Norbornene-2-carbonitrile 95-12-5, 5-Norbornene-2-methanol 95-14-7, 1H-Benzotriazole 95-15-8, Thionaphthene 95-16-9, Benzothiazole 95-20-5, 2-Methylindole 95-21-6, 2-Methylbenzoxazole 95-25-0, Chlorzoxazone 95-96-5, 3,6-Dimethyl-1,4-dioxane-2,5-dione 96-45-7, 2-Imidazolidinethione 96-48-0 96-50-4, 2-Aminothiazole 97-59-6, 5-Ureidohydantoin 98-02-2, Furfurylmercaptan 98-04-4, Phenyl trimethyl ammonium iodide 98-79-3 98-96-4, Pyrazinecarboxamide 100-26-5, 2,5-Pyridine dicarboxylic acid 100-64-1, Cyclohexanone oxime 101-02-0, Triphenylphosphite 101-68-8 102-85-2, Tributylphosphite 103-76-4, 1-(2-Hydroxyethyl)piperazine 104-50-7 104-67-6 104-74-5, 1-Dodecylpyridinium chloride 105-55-5, 1,3-Diethyl-2-thiourea 105-60-2, uses 105-81-7 106-02-5, Oxacyclohexadecan-2-one 107-29-9, Acetaldoxime 108-27-0 108-29-2 108-31-6, Maleic anhydride, uses 108-33-8 108-49-6, 2,6-Dimethylpiperazine 108-52-1 108-55-4, Glutaric anhydride 108-74-7, 1,3,5-Trimethylhexahydro-1,3,5-triazine 108-77-0, Cyanuric chloride 108-80-5, Cyanuric acid 108-94-1, Cyclohexanone, uses 108-97-4, 4H-Pyran-4-one 109-01-3, 1-Methylpiperazine 109-05-7, 2-Methylpiperidine 109-12-6, 2-Aminopyrimidine 109-46-6, 1,3-Dibutyl-2-thiourea 109-57-9, 1-Allyl-2-thiourea 110-61-2, Succinonitrile 110-88-3, 1,3,5-Trioxane, uses 110-89-4, Piperidine, uses 111-49-9, Homopiperidine 112-02-7, Palmityl trimethyl ammonium chloride 112-03-8, Stearyl trimethyl ammonium chloride 113-52-0, Imipramine hydrochloride 115-86-6, Triphenoxyphosphine oxide 118-00-3, Guanosine, uses 119-44-8, Xanthopterin 119-51-7, 1-Phenyl-1,2-propanedione 2-oxime 119-84-6 120-57-0, Piperonal 120-72-9, Indole, uses 120-73-0,

Purine 120-75-2, 2-Methylbenzothiazole 120-93-4, 2-Imidazolidone 121-45-9, Trimethylphosphite 121-54-0, Benzethonium chloride 121-66-4, 2-Amino-5-nitrothiazole 122-18-9, Benzylcetyldimethylammonium chloride 122-19-0, Benzylstearyldimethylammonium chloride 122-52-1, Triethyl phosphite 122-96-3, 1,4-Bis(2-hydroxyethyl)piperazine 123-00-2, 4-(3-Aminopropyl)morpholine 123-03-5, Acetoquat CPC 123-56-8, Succinimide 124-03-8, Cetyl dimethyl ethyl ammonium bromide 126-33-0, Tetramethylenesulfone 126-54-5, 2,4,8.10-Tetraoxaspiro[5.5]undecane 127-06-0, Acetone oxime 127-63-9, Phenylsulfone 127-69-5, Sulfisoxazole 128-53-0 130-61-0, Thioridazine hydrochloride 133-32-4, 3-Indolebutyric acid 134-31-6 136-85-6 138-24-9, Phenyl trimethyl ammonium chloride 139-07-1, Dodecyl benzyl dimethyl ammonium chloride 139-08-2, Benzyltetradecyldimethylammonium chloride 140-08-9, Tris(2-chloroethyl)phosphite 140-31-8, 1-(2-Aminoethyl)piperazine 140-72-7, Acetoquat CPB 140-87-4, Cyanoacetohydrazide 141-30-0, 3,6-Dichloropyridazine 141-90-2, 2-Thiouracil 141-94-6, Hexetidine 144-35-4 146-68-9 146-80-5, Xanthosine 147-85-3, Proline, uses 148-24-3, 8-Hydroxyquinoline, uses 149-29-1, Patulin 150-60-7, Benzyl disulfide 153-98-0, Serotonin hydrochloride 154-69-8, Tripelennamine hydrochloride 154-97-2 155-54-4, Hydroorotic acid 156-83-2, 2,6-Diamino-4-chloropyrimidine 177-10-6, 1,4-Dioxaspiro[4.5]**decane** 177-11-7, 4-Piperidone ethylene ketal 180-84-7, 1,7-Dioxaspiro[5.5]undecane 183-97-1, 1,4-Cyclohexanedione bis(ethylene ketal) 230-27-3, 7,8-Benzoquinoline 230-46-6, 1,7-Phenanthroline 253-52-1, Phthalazine 271-44-3, Indazole 271-58-9, 2,1-Benzisoxazole 271-63-6, 7-Azaindole 271-95-4, 1,2-Benzisoxazole 273-13-2, 2,1,3-Benzothiadiaazole 273-53-0, Benzoxazole 275-51-4, Azulene 279-23-2, Norbornane 286-62-4, Cyclooctene oxide 286-75-9, 1,2,5,6-Diepoxyoctane 286-99-7, 13-Oxabicyclo[10.1.0]tridecane 288-13-1, Pyrazole 288-32-4, Imidazole, uses 288-36-8, 1,2,3-Triazole 288-88-0, 1H-1,2,4-Triazole 288-94-8, 1H-Tetrazole 289-80-5, Pyridazine 289-95-2, Pyrimidine 290-37-9, Pyrazine 290-87-9, 1,3,5-Triazine 291-21-4, 1,3,5-Trithiane 294-80-4, 1,5,9-Triazacyclododecane 294-90-6, 1,4,7,10-Tetraazacyclododecane 294-93-9, 1,4,7,10-Tetraoxacyclododecane 295-37-4, 1,4,8,11-Tetraazacyclotetradecane 295-91-0, 1,5,9,13-Tetrathiacyclohexadecane 296-41-3, 1,4,7,10,13,16-Hexathiacyclooctadecane 298-46-4, Carbamazepine 298-96-4 299-11-6, Phenazine methosulfate 300-68-5, Tremorine dihydrochloride 303-26-4, 1-(4-Chlorobenzhydryl)piperazine 304-88-1 305-33-9, Iproniazid phosphate 306-44-5, Pyruvaldehyde-1-oxime 311-28-4, Tetrabutyl ammonium iodide 312-45-8, Hemicholinium-3 315-30-0, 4-Hydroxypyrazolo[3,4-d]pyrimidine 321-30-2 326-61-4, Piperonyl acetate 343-27-1,

Harmine hydrochloride 343-94-2, Tryptamine hydrochloride 363-11-1, Harmaline hydrochloride 373-68-2, Tetramethylammonium fluoride 383-29-9, 4-(Fluorophenyl)sulfone (transparentizing agent for electrophotog. migration imaging members)

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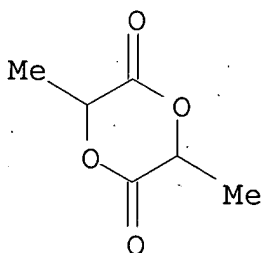
120:134495 Continuous process for the production of cyclic esters from hydroxyacids or their derivatives. Benecke, Herman P.; Cheung, Alex; Cremeans, George E.; Hillman, Melville E. D.; Lipinsky, Edward S.; Markle, Richard A.; Sinclair, Richard G. (Biopak Technology Ltd., USA). PCT Int. Appl. WO 9319058 A2 19930930, 142 pp. DESIGNATED STATES: W: AT, AU, BB, BG, BR, CA, CH, DE, DK, ES, FI, GB, HU, JP, KP, KR, LK, LU, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, UA; RW: AT, BE, BF, BJ, CF, CG, CH, CI, CM, DE, DK, ES, FR, GA, GB, GR, IE, IT, LU, MC, ML, MR, NL, PT, SE, SN, TD, TG. (English). CODEN: PIXXD2. APPLICATION: WO 1993-US2483 19930317. PRIORITY: US 1992-854559 19920319.

AB Cyclic esters of hydroxyacids are prep'd. continuously in a process which avoids the need for expensive product purifn. A feedstream comprising the hydroxyacid and its dimer are dild. in an org. solvent and water is removed from feedstream to directly form a cyclic ester from the acid dimer. A process schematic is presented. Thus, com. lactic acid was dissolved in PhMe to produced a 5% lactic acid soln., Dowex-50 H<sup>+</sup> ion exchange resin added, the reaction heated, and free water removed, producing **lactide** in .apprx.13% yield.

IT **95-96-5P, Lactide**  
(prepn. of, continuous process for)

RN 95-96-5 HCA

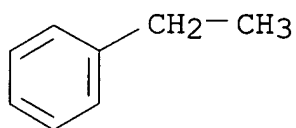
CN 1,4-Dioxane-2,5-dione, 3,6-dimethyl- (9CI) (CA INDEX NAME)



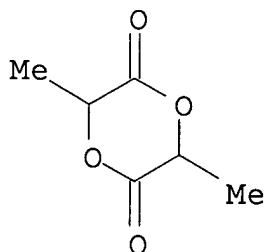
IT **100-41-4, uses**  
(solvents, in cyclization of hydroxyacids)

RN 100-41-4 HCA

CN Benzene, ethyl- (7CI, 8CI, 9CI) (CA INDEX NAME)



- IC ICM C07D319-12  
ICS C07D323-04
- CC 28-11 (Heterocyclic Compounds (More Than One Hetero Atom))  
Section cross-reference(s): 48
- ST cyclic ester continuous prepn; **lactide** prepn lactic acid  
cyclization; hydroxyacid esterification cyclic ester prepn;  
lactonization hydroxyacid continuous
- IT **95-96-5P, Lactide**  
(prepn. of, continuous process for)
- IT 98-82-8, Cumene **100-41-4**, uses 25551-13-7,  
Trimethylbenzene  
(solvents, in cyclization of hydroxyacids)
- L34 ANSWER 8 OF 14 HCA COPYRIGHT 2005 ACS on STN
- 118:88646 Heat capacities and entropies of organic compounds in the  
condensed phase. Volume II. Domalski, Eugene S.; Hearing,  
Elizabeth D. (Cent. Chem. Phys., Natl. Inst. Stand. Technol.,  
Gaithersburg, MD, 20899, USA). Journal of Physical and Chemical  
Reference Data, 19(4), 881-1047 (English) 1990. CODEN: JPCRBU.  
ISSN: 0047-2689.
- AB A review with 565 refs. including heat capacities, entropies, and  
thermodn. parameters for phase transitions for >1100 org. compds.
- IT **95-96-5, DL-Lactide 112-40-3,**  
**Dodecane 124-18-5, Decane**  
**502-97-6, 1,4-Dioxane-2,5-dione**  
(thermodn. properties of)
- RN 95-96-5 HCA
- CN 1,4-Dioxane-2,5-dione, 3,6-dimethyl- (9CI) (CA INDEX NAME)



- RN 112-40-3 HCA
- CN Dodecane (8CI, 9CI) (CA INDEX NAME)

Me- (CH<sub>2</sub>)<sub>10</sub>-Me

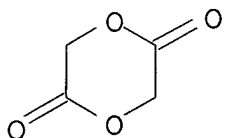
RN 124-18-5 HCA

CN Decane (8CI, 9CI) (CA INDEX NAME)

Me- (CH<sub>2</sub>)<sub>8</sub>-Me

RN 502-97-6 HCA

CN 1,4-Dioxane-2,5-dione (9CI) (CA INDEX NAME)



CC 69-0 (Thermodynamics, Thermochemistry, and Thermal Properties)

Section cross-reference(s): 22

IT 50-21-5, properties 50-69-1, D-Ribose 50-70-4, D-Glucitol, properties 50-99-7, D-Glucose, properties 51-17-2, Benzimidazole 51-28-5, 2,4-Dinitrophenol, properties 51-79-6, Urethane 51-98-9 56-12-2, properties 56-23-5, Tetrachloromethane, properties 56-33-7, 1,1,3,3-Tetramethyl-1,3-diphenyldisiloxane 56-81-5, 1,2,3-Propanetriol, properties 56-86-0, Glutamic acid, properties 57-11-4, Octadecanoic acid, properties 57-13-6, Urea, properties 57-14-7 57-48-7, D-Fructose, properties 57-50-1, Sucrose, properties 57-55-6, 1,2-Propanediol, properties 57-56-7, Semicarbazide 57-57-8, .beta.-Propiolactone 58-08-2, Caffeine, properties 58-86-6, D-Xylose, properties 58-95-7, .alpha.-Tocopherol acetate 59-23-4, D-Galactose, properties 59-51-8, DL-Methionine 60-01-5, Tributyrin 60-32-2, 6-Aminohexanoic acid 60-35-5, Acetamide, properties 61-90-5, L-Leucine, properties 62-23-7, 4-Nitrobenzoic acid 62-53-3, Aniline, properties 62-55-5, Thioacetamide 62-56-6, Thiourea, properties 63-42-3 63-68-3, L-Methionine, properties 64-10-8, Phenylurea 64-17-5, Ethanol, properties 64-19-7, Acetic acid, properties 65-71-4, Thymine 65-85-0, Benzoic acid, properties 66-56-8, 2,3-Dinitrophenol 67-52-7, Barbituric acid 67-56-1, Methanol, properties 67-66-3, Chloroform, properties 67-72-1, Hexachloroethane 68-12-2, DMF, properties 68-22-4 69-09-0, Chlorpromazine hydrochloride 69-65-8, D-Mannitol 69-79-4, Maltose 71-23-8, 1-Propanol, properties 71-36-3, 1-Butanol, properties 71-41-0, 1-Pentanol, properties 71-43-2, Benzene, properties 71-55-6, 1,1,1-Trichloroethane 74-82-8, Methane, properties 74-84-0, Ethane, properties 74-85-1, Ethene,



properties 74-98-6, Propane, properties 75-01-4, properties 75-05-8, Acetonitrile, properties 75-07-0, Ethanal, properties 75-09-2, properties 75-12-7, Formamide, properties 75-24-1, Trimethylaluminum 75-25-2, Bromoform 75-37-6, 1,1-Difluoroethane 75-56-9, properties 75-63-8, Bromotrifluoromethane 75-65-0, 2-Methyl-2-propanol, properties 75-69-4, Fluorotrichloromethane 75-73-0, Tetrafluoromethane 75-74-1, Tetramethyllead 75-77-4, properties 75-78-5, Dichlorodimethylsilane 75-79-6, Trichloromethylsilane 75-83-2, 2,2-Dimethylbutane 75-85-4, 2-Methyl-2-butanol 75-97-8 76-03-9, Trichloroacetic acid, properties 76-11-9 76-13-1, Freon 113 76-86-8, Triphenylchlorosilane 77-09-8, Phenolphthalein 77-63-4 77-74-7, 3-Methyl-3-pentanol 77-76-9, 2,2-Dimethoxypropane 77-92-9, properties 77-99-6 78-00-2, Tetraethyllead 78-67-1 78-83-1, 2-Methyl-1-propanol, properties 78-92-2, 2-Butanol 78-93-3, Methyl ethyl ketone, properties 79-00-5, 1,1,2-Trichloroethane 79-01-6, Trichloroethene, properties 79-09-4, Propanoic acid, properties 79-10-7, 2-Propenoic acid, properties 79-11-8, Chloroacetic acid, properties 79-19-6, Thiosemicarbazide 79-29-8, 2,3-Dimethylbutane 79-31-2, Isobutyric acid 79-34-5, 1,1,2,2-Tetrachloroethane 79-38-9, Chlorotrifluoroethene 79-41-4, properties 79-43-6, Dichloroacetic acid, properties 80-05-7, properties 80-07-9 80-08-0 80-62-6 82-71-3, 2,4,6-Trinitroresorcinol 84-74-2, Dibutyl phthalate 85-01-8, Phenanthrene, properties 85-42-7 85-44-9, 1,3-Isobenzofurandione 87-52-5, Gramine 87-62-7, 2,6-Dimethylaniline 87-65-0, 2,6-Dichlorophenol 87-85-4, Hexamethylbenzene 87-89-8, myo-Inositol 88-65-3, 2-Bromobenzoic acid 88-73-3, 1,2-Chloronitrobenzene 88-75-5, 2-Nitrophenol 88-89-1, Picric acid 89-32-7, Pyromellitic dianhydride 90-13-1, 1-Chloronaphthalene 90-98-2 91-15-6, Phthalonitrile 91-20-3, Naphthalene, properties 91-22-5, Quinoline, properties 91-58-7, 2-Chloronaphthalene 92-51-3, Bicyclohexyl 92-52-4, Biphenyl, properties 92-88-6, [1,1'-Biphenyl]-4,4'-diol 92-94-4, p-Terphenyl 95-14-7, 1H-Benzotriazole 95-48-7, properties 95-50-1, 1,2-Dichlorobenzene 95-57-8, 2-Chlorophenol 95-65-8, 3,4-Dimethylphenol 95-77-2, 3,4-Dichlorophenol 95-87-4, 2,5-Dimethylphenol 95-94-3, 1,2,4,5-Tetrachlorobenzene 95-96-5, DL-Lactide 96-14-0, 3-Methylpentane 96-22-0, 3-Pentanone 96-31-1, 1,3-Dimethylurea 96-33-3 96-48-0 96-54-8, N-Methylpyrrole 97-53-0 97-88-1 97-93-8, Triethylaluminum, properties 97-94-9 98-07-7, Benzotrichloride 98-46-4, 3-(Trifluoromethyl)nitrobenzene 98-83-9, properties 98-95-3, Nitrobenzene, properties 99-09-2, 3-Nitroaniline 99-65-0, 1,3-Dinitrobenzene 100-00-5, 4-Nitrochlorobenzene 100-01-6, 4-Nitroaniline, properties 100-02-7, 4-Nitrophenol, properties 100-17-4, p-Nitroanisole 100-20-9, 1,4-Benzenedicarbonyl dichloride 100-25-4, 1,4-Dinitrobenzene

100-29-8, p-Nitrophenetole 100-42-5, properties 100-47-0, Benzonitrile, properties 100-61-8, N-Methylaniline, properties 100-63-0, Phenylhydrazine 100-66-3, Anisole, properties 101-68-8 101-77-9 101-80-4 101-81-5, Diphenylmethane 102-07-8, 1,3-Diphenylurea 102-54-5, Ferrocene 102-67-0, Tripropylaluminum 102-71-6, Triethanolamine, properties 102-76-1, Glycerol triacetate 103-23-1 103-24-2 103-29-7, 1,2-Diphenylethane 103-30-0, trans-Stilbene 103-33-3, Azobenzene 103-73-1, Ethyl phenyl ether 103-84-4, Acetanilide 104-76-7, 2-Ethylhexanol 104-94-9, p-Anisidine 105-16-8 105-30-6, 2-Methyl-1-pentanol 105-37-3, Ethyl propanoate 105-56-6, Ethyl cyanoacetate 105-60-2, properties 105-67-9, 2,4-Dimethylphenol 105-68-0, Isoamyl propionate 105-72-6 106-36-5, Propyl propanoate 106-37-6, 1,4-Dibromobenzene 106-39-8, 4-Chlorobromobenzene 106-41-2, 4-Bromophenol 106-42-3, properties 106-44-5, properties 106-46-7, 1,4-Dichlorobenzene 106-48-9, 4-Chlorophenol 106-49-0, 4-Methylaniline, properties 106-57-0, 2,5-Dioxopiperazine 106-93-4, 1,2-Dibromoethane 106-98-9, 1-Butene, properties 107-06-2, 1,2-Dichloroethane, properties 107-15-3, 1,2-Ethanediamine, properties 107-21-1, 1,2-Ethandiol, properties 107-31-3, Methyl formate 107-83-5, 2-Methylpentane 107-87-9, 2-Pentanone 107-91-5, Cyanoacetamide 107-95-9, .beta.-Alanine 108-10-1, 4-Methyl-2-pentanone 108-11-2 108-31-6, 2,5-Furandione, properties 108-32-7 108-36-1, 1,3-Dibromobenzene 108-37-2, 3-Chlorobromobenzene 108-39-4, properties 108-43-0, 3-Chlorophenol 108-45-2, 1,3-Benzenediamine, properties 108-46-3, Resorcinol, properties 108-47-4, 2,4-Dimethylpyridine 108-48-5, 2,6-Dimethylpyridine 108-68-9, 3,5-Dimethylphenol 108-80-5, 1,3,5-Triazine-2,4,6(1H,3H,5H)-trione 108-83-8, 2,6-Dimethyl-4-heptanone 108-86-1, Bromobenzene, properties 108-87-2, Methylcyclohexane 108-88-3, Toluene, properties 108-89-4, 4-Methylpyridine 108-90-7, Chlorobenzene, properties 108-94-1, Cyclohexanone, properties 108-95-2, Phenol, properties

(thermodn. properties of)

IT 109-05-7, 2-Methylpiperidine 109-06-8, 2-Methylpyridine 109-21-7, Butyl butanoate 109-55-7, N,N-Dimethyl-1,3-propanediamine 109-60-4, Propyl acetate 109-67-1, 1-Pentene 109-69-3, 1-Chlorobutane 109-77-3, Malononitrile 109-79-5, 1-Butanethiol 109-99-9, properties 110-02-1, Thiophene 110-49-6, 2-Methoxyethanol acetate 110-54-3, Hexane, properties 110-56-5, 1,4-Dichlorobutane 110-58-7, Pentylamine 110-59-8, Pentanenitrile 110-61-2, Succinonitrile 110-62-3, Valeraldehyde 110-63-4, 1,4-Butanediol, properties 110-74-7, Propyl formate 110-82-7, Cyclohexane, properties 110-83-8, Cyclohexene, properties 110-85-0, Piperazine, properties 110-88-3, 1,3,5-Trioxane, properties 110-89-4, Piperidine, properties 110-91-8, Morpholine, properties 110-93-0, 6-Methyl-5-hepten-2-one

110-96-3, Diisobutylamine 111-15-9, 2-Ethoxyethanol acetate  
111-27-3, 1-Hexanol, properties 111-31-9, 1-Hexanethiol  
111-40-0, Diethylenetriamine 111-42-2, properties 111-46-6,  
Diethylene glycol, properties 111-55-7, Ethylene glycol diacetate  
111-65-9, Octane, properties 111-70-6, Heptyl alcohol 111-71-7,  
Heptanal 111-76-2, 3-Oxa-1-heptanol 111-78-4,  
Cycloocta-1,5-diene 111-84-2, Nonane 111-87-5, 1-Octanol,  
properties 111-88-6, 1-Octanethiol 111-96-6, Diglyme 112-24-3  
112-27-6 112-31-2, Decanal 112-34-5, 2-(2-Butoxyethoxy)ethanol  
**112-40-3, Dodecane** 112-55-0, 1-Dodecanethiol  
112-57-2, Tetraethylenepentamine 112-60-7, Tetraethylene glycol  
112-95-8, Eicosane 113-59-7, Chlorprothixene 115-07-1,  
1-Propene, properties 115-11-7, Isobutene, properties 115-18-4,  
2-Methyl-3-buten-2-ol 115-25-3, Octafluorocyclobutane 115-77-5,  
Pentaerythritol, properties 115-86-6 116-11-0,  
2-Methoxy-1-propene 117-81-7, Di(2-ethylhexyl) phthalate  
117-84-0, Dioctyl phthalate 118-79-6, 2,4,6-Tribromophenol  
119-61-9, Benzophenone, properties 119-65-3, Isoquinoline  
120-72-9, 1H-Indole, properties 120-80-9, 1,2-Dihydroxybenzene,  
properties 120-82-1, 1,2,4-Trichlorobenzene 120-83-2,  
2,4-Dichlorophenol 121-46-0, Bicyclo[2.2.1]hepta-2,5-diene  
122-60-1, Phenyl glycidyl ether 122-96-3, 1,4-Piperazinediethanol  
123-31-9, Hydroquinone, properties 123-38-6, Propanal, properties  
123-39-7, N-Methylformamide 123-80-8 123-86-4, Butyl acetate  
123-91-1, 1,4-Dioxane, properties 123-95-5, Butyl octadecanoate  
124-04-9, Hexanedioic acid, properties 124-13-0, Octanal  
**124-18-5, Decane** 124-19-6, Nonanal 124-70-9,  
Dichloromethylvinylsilane 124-73-2, 1,2-Dibromotetrafluoroethane  
126-73-8, Tributyl phosphate, properties 127-09-3 127-18-4,  
Tetrachloroethene, properties 129-64-6 131-11-3, Dimethyl  
phthalate 132-65-0, Dibenzothiophene 134-81-6, Benzil 135-70-6  
, p-Quaterphenyl 137-40-6, Sodium propanoate 139-42-4  
139-45-7, Tripropionin 139-85-5, 3,4-Dihydroxybenzaldehyde  
140-31-8, N-(2-Aminoethyl)piperazine 141-10-6 141-22-0,  
Ricinoleic acid 141-32-2 141-53-7, Sodium formate 141-78-6,  
Ethyl acetate, properties 142-72-3, Magnesium acetate 142-82-5,  
Heptane, properties 142-84-7, Dipropylamine 142-92-7, Hexyl  
ethanoate 142-96-1, Dibutyl ether 143-10-2, 1-Decanethiol  
147-82-0, 2,4,6-Tribromoaniline 151-67-7 191-48-0, Decacyclene  
229-87-8, Phenanthridine 230-27-3, 7,8-Benzoquinoline 238-84-6,  
1,2-Benzofluorene 243-17-4, 2,3-Benzofluorene 246-42-4  
260-94-6, Acridine 271-44-3, Indazole 271-89-6, 2,3-Benzofuran  
278-06-8, Quadricyclane 279-19-6, Nortricyclene 279-23-2,  
Norbornane 283-56-7, Triethanolamine borate 286-20-4,  
Cyclohexene oxide 288-13-1, Pyrazole 288-32-4, Imidazole,  
properties 288-88-0, 1H-1,2,4-Triazole 292-64-8, Cyclooctane  
295-37-4, Cyclam 296-18-4, Cyclooctadecane 303-43-5, Cholesteryl  
oleate 323-09-1, 2-Fluoronaphthalene 327-57-1, L-Norleucine

327-62-8, Potassium propionate 329-71-5, 2,5-Dinitrophenol  
334-48-5, Decanoic acid 335-57-9, Perfluoroheptane 352-32-9,  
4-Fluorotoluene 354-06-3, 1-Bromo-2-chloro-1,1,2-trifluoroethane  
354-34-7, Trifluoroacetyl fluoride 354-58-5, 1,1,1-  
Trichlorotrifluoroethane 355-25-9 355-42-0, Perfluorohexane  
356-24-1, Methyl perfluorobutanoate 359-40-0, Oxalyl fluoride  
359-70-6, Perfluorotriethylamine 367-11-3, 1,2-Difluorobenzene  
372-18-9, 1,3-Difluorobenzene 375-42-8, 1,4-Dibromo-2,3-  
dichlorohexafluorobutane 392-56-3, Hexafluorobenzene 398-23-2,  
4,4'-Difluorobiphenyl 420-04-2, Cyanamide 434-90-2,  
Decafluorobiphenyl 454-92-2, 3-Trifluoromethylbenzoic acid  
462-06-6, Fluorobenzene 477-75-8, Triptycene 487-89-8,  
3-Indolealdehyde 493-01-6, cis-Decalin 493-02-7, trans-Decalin  
493-05-0, Isochroman 493-08-3, Chroman 493-77-6,  
Triphenyl-s-triazine 498-66-8, Bicyclo[2.2.1]heptene 501-52-0,  
Benzenepropanoic acid 501-65-5, Diphenylacetylene 502-44-3,  
2-Oxepanone 502-56-7, 5-Nonanone 502-97-6,  
1,4-Dioxane-2,5-dione 505-23-7, 1,3-Dithiane 505-29-3,  
1,4-Dithiane 505-32-8, Isophytol 513-29-1, Triglycine sulfate  
513-29-1D, solid soln. with triglycine selenate 513-35-9,  
2-Methyl-2-butene 520-03-6, N-Phenylphthalimide 526-75-0  
528-29-0, 1,2-Dinitrobenzene 536-74-3, Phenylacetylene 540-18-1,  
Pentyl butanoate 540-36-3, 1,4-Difluorobenzene 540-84-1,  
2,2,4-Trimethylpentane 541-73-1, 1,3-Dichlorobenzene 542-11-0,  
Aniline hydrobromide 542-28-9, .delta.-Valerolactone 542-59-6,  
Ethylene glycol acetate 542-92-7, Cyclopentadiene, properties  
544-76-3, Hexadecane 544-85-4, Dotriacontane 544-97-8,  
Dimethylzinc 546-44-1 546-56-5, Octaphenylcyclotetrasiloxane  
554-12-1, Methyl propanoate 554-84-7, 3-Nitrophenol 555-43-1,  
Tristearin 556-67-2 557-17-5, Methyl n-propyl ether 557-20-0,  
Diethylzinc 557-34-6, Zinc acetate 558-13-4, Tetrabromomethane  
562-49-2, 3,3-Dimethylpentane 563-45-1, 3-Methyl-1-butene  
563-46-2, 2-Methyl-1-butene 563-68-8, Thallium acetate 563-80-4,  
Isopropyl methyl ketone 563-83-7, 2-Methylpropanamide 565-59-3,  
2,3-Dimethylpentane 565-60-6, 3-Methyl-2-pentanol 573-56-8,  
2,6-Dinitrophenol 576-24-9, 2,3-Dichlorophenol 576-26-1,  
2,6-Dimethylphenol 577-71-9, 3,4-Dinitrophenol 580-35-8  
581-40-8, 2,3-Dimethylnaphthalene 583-53-9, 1,2-Dibromobenzene  
583-55-1, 2-Bromiodobenzene 583-58-4, 3,4-Dimethylpyridine  
583-61-9, 2,3-Lutidine 583-78-8, 2,5-Dichlorophenol 585-76-2,  
3-Bromobenzoic acid 586-11-8, 3,5-Dinitrophenol 586-76-5,  
4-Bromobenzoic acid 589-38-8, 3-Hexanone 589-39-9, Potassium  
butyrate 589-87-7, 4-Bromiodobenzene 589-93-5,  
2,5-Dimethylpyridine 590-18-1, cis-2-Butene 591-18-4 591-22-0,  
3,5-Dimethylpyridine 591-35-5, 3,5-Dichlorophenol 591-47-9,  
4-Methylcyclohexene 591-68-4 591-78-6, 2-Hexanone 592-31-4,  
Butylurea 592-41-6, 1-Hexene, properties 592-84-7, Butyl  
methanoate 593-45-3, Octadecane 593-49-7, Heptacosane

593-88-4, Trimethylarsine 594-27-4, Tetramethylstannane  
 (thermodn. properties of)

IT 595-49-3, 2,2-Dinitropropane 597-63-7, Tetraethylgermane  
 597-64-8, Tetraethyltin 598-50-5, Methylurea 598-55-0, Methyl  
 carbamate 598-94-7, 1,1-Dimethylurea 601-34-3, Cholesteryl  
 palmitate 603-35-0, Triphenylphosphine, properties 604-45-5,  
 Hexaphenylisomelamine 604-88-6, Hexaethylbenzene 605-39-0,  
 2,2'-Dimethylbiphenyl 608-66-2, Galactitol 612-71-5,  
 1,3,5-Triphenylbenzene 612-78-2, .beta.,.beta.'-Binaphthyl  
 613-31-0, 9,10-Dihydroanthracene 615-42-9, 1,2-Diiodobenzene  
 616-06-8, DL-Norleucine 616-45-5, .alpha.-Pyrrolidone 621-82-9,  
 properties 622-16-2, Diphenylcarbodiimide 623-26-7,  
 1,4-Dicyanobenzene 623-76-7, 1,3-Diethylurea 624-38-4,  
 1,4-Diiodobenzene 624-54-4, Pentyl propionate 624-64-6,  
 trans-2-Butene 625-52-5, Ethylurea 625-82-1, 2,4-Dimethylpyrrole  
 625-84-3, 2,5-Dimethylpyrrole 626-00-6, 1,3-Diiodobenzene  
 627-06-5, Propylurea 627-20-3, cis-2-Pentene 627-44-1,  
 Diethylmercury 628-28-4, Methyl butyl ether 628-32-0, Ethyl  
 propyl ether 628-36-4, Diformylhydrazine 628-92-2, Cycloheptene  
 629-11-8, 1,6-Hexanediol 629-14-1, 3,6-Dioxaoctane 629-59-4,  
 Tetradecane 629-62-9, Pentadecane 629-78-7, Heptadecane  
 629-92-5, Nonadecane 629-94-7, Heneicosane 629-97-0, Docosane  
 629-99-2, Pentacosane 630-01-3, Hexacosane 630-02-4, Octacosane  
 630-03-5, Nonacosane 630-06-8, Hexatriacontane 630-19-3,  
 Pivalaldehyde 631-36-7, Tetraethylsilicon 632-14-4,  
 1,1,3-Trimethylurea 632-22-4, Tetramethylurea 634-95-7,  
 1,1-Diethylurea 635-46-1, 1,2,3,4-Tetrahydroquinoline 637-88-7,  
 1,4-Cyclohexanedione 638-67-5, Tricosane 638-68-6, Triacontane  
 646-04-8, trans-2-Pentene 646-06-0, 1,3-Dioxolane 646-31-1,  
 Tetracosane 660-88-8, 5-Aminopentanoic acid 673-66-5,  
 .zeta.-Enantholactam 675-20-7, .alpha.-Piperidone 678-26-2,  
 Perfluoropentane 680-31-9, Hexamethylphosphoric triamide,  
 properties 681-84-5, Tetramethyl silicate 691-60-1,  
 Isopropylurea 694-80-4, 2-Chlorobromobenzene 700-13-0,  
 Trimethylhydroquinone 700-57-2, 2-Hydroxyadamantane 713-36-0,  
 Phenyl-o-tolylmethane 740-98-7 754-05-2, Vinyltrimethylsilane  
 754-10-9, 2,2-Dimethylpropanamide 758-48-5 768-95-6,  
 1-Hydroxyadamantane 776-35-2, 9,10-Dihydrophenanthrene 791-28-6,  
 Triphenylphosphine oxide 797-77-3 822-06-0 827-52-1,  
 Cyclohexylbenzene 832-64-4, 4-Methylphenanthrene 865-52-1,  
 Tetramethylgermane 874-14-6, 1,3-Dimethyluracil 920-25-2D, solid  
 soln. with triglycine sulfate 927-49-1, 6-Undecanone 927-83-3  
 931-88-4, Cyclooctene 992-98-3, Thallium formate 1002-57-9,  
 8-Aminooctanoic acid 1005-51-2, Bullvalene 1013-08-7,  
 1,2,3,4-Tetrahydrophenanthrene 1020-84-4 1067-20-5,  
 3,3-Diethylpentane 1070-87-7, 2,2,4,4-Tetramethylpentane  
 1071-22-3, .beta.-(Trichlorosilyl)propionitrile 1074-29-9,  
 Phenyltrichlorogermane 1079-71-6, 1,2,3,4,5,6,7,8-

Octahydroanthracene 1118-12-3, tert-Butylurea 1120-56-5,  
Methylenecyclobutane 1124-19-2, Phenyltrichlorostannane  
1125-26-4 1156-51-0, 2,2-Bis(4-cyanatophenyl)propane 1223-66-1  
1226-26-2 1247-08-1, Triphenyl(phenylethynyl)tin 1271-24-5,  
Chromocene 1271-28-9, Nickelocene 1271-54-1 1277-43-6,  
Cobaltocene 1277-47-0, Vanadocene 1287-13-4, Ruthenocene  
1294-07-1, (Tricyclopentadienyl)yttrium 1330-78-5, Tricresyl  
phosphate 1445-79-0, Trimethylgallium 1450-14-2,  
Hexamethyldisilane 1451-99-6, Octaethylcyclotetrasiloxane  
1484-12-4, N-Methylcarbazole 1486-01-7, Biphenyl-d10 1492-24-6  
1522-20-9, Acetylacetone enol 1562-94-3, p-Azoxyanisole  
1603-53-8 1604-32-6 1604-34-8, 6,10-Dimethyl-2-undecanone  
1604-35-9 1627-98-1, 1,1,3,3-Tetramethyl-1,3-disilacyclobutane  
1627-99-2, 1,1,3,3,5,5-Hexamethyl-1,3,5-trisilacyclohexane  
1633-22-3, 2,2-Paracyclophane 1634-04-4, Methyl tert-butyl ether  
1675-54-3 1675-57-6, Diphenyldiethynylsilane 1675-59-8,  
Diethynyldiphenylgermane 1693-44-3 1693-46-5 1693-51-2  
1712-64-7, Isopropyl nitrate 1725-04-8, Tridecanolactone  
1755-01-7, endo-Dicyclopentadiene 1769-41-1, Isonitrosoacetanilide  
1792-17-2, N,N'-Dibutylurea 1812-51-7, 2-Ethylbiphenyl  
1836-75-5, 2,4-Dichloro-4'-nitrodiphenyl ether 1888-94-4  
1889-67-4, 2,3-Dimethyl-2,3-diphenylbutane 1989-52-2, Cholesteryl  
myristate 2031-79-0, 1,1,3,3,5,5-Hexaethylcyclotrisiloxane  
2051-24-3, Decachlorobiphenyl 2051-62-9, p-Chlorobiphenyl  
2079-95-0, 1-Tetradecanethiol 2094-99-7 2117-28-4 2117-48-8,  
Triphenylvinyltin 2141-42-6, 1,2,3,4-Tetrahydroanthracene  
2157-01-9, Octyl methacrylate 2163-00-0, 1,6-Dichlorohexane  
2195-84-8 2227-79-4, Thiobenzamide 2231-57-4, Thiocarbohydrazide  
2295-05-8, 1,3-Bis(trimethylsilyl)propane 2295-12-7,  
1,1-Dimethyl-1-silacyclobutane 2296-13-1 2296-14-2,  
Dioctylammonium chloride 2396-72-7, Triglycine fluoroberyllate  
2416-94-6 2438-40-6, Trimargarin 2449-10-7, Dihexyl sebacate  
2483-57-0, Methyl nitroacetate 2486-84-2 2615-15-8, Hexaethylene  
glycol 2622-67-5, 1,2-Diphenylbenzimidazole 2664-55-3, Nonyl  
acrylate 2676-59-7, 3,3',4,4'-Tetraaminodiphenyl ether  
2691-41-0, HMX 2778-41-8 2778-42-9 2809-69-0, 2,4-Hexadiyne  
2825-82-3, exo-Tetrahydrodicyclopentadiene 2867-47-2 2885-00-9,  
1-Octadecanethiol 2892-51-5, Squaric acid 2893-43-8,  
Methylethylethanolamine 2917-26-2, 1-Hexadecanethiol 3073-05-0,  
p-Quinquephenyl 3179-47-3, Decylmethacrylate 3244-41-5  
3363-97-1 3424-57-5 3458-28-4, D-Mannose 3515-93-3,  
.beta.-Cyanopropionaldehyde 3524-70-7, Ethylene oxalate  
3836-23-5 3938-95-2, Ethyl 2,2-dimethylpropanoate 4170-30-3,  
Crotonaldehyde 4316-37-4, Acetophenone diethyl ketal 4390-04-9,  
2,2,4,4,6,8,8-Heptamethylnonane 4727-29-1, Phthalanilic acid  
5160-53-2 5171-91-5 5219-48-7 5219-49-8 5256-77-9, Copper  
vinylacetylenide 5328-37-0, L-Arabinose 5332-73-0,  
3-Methoxypropylamine 5392-40-5, Citral 5511-18-2,

Tricyclo[3.3.1.1<sup>3</sup>,7]decane-1-carboxamide 5743-97-5,  
 Perhydrophenanthrene 5794-28-5, Calcium oxalate monohydrate  
 5892-42-2 5893-61-8, Copper (II) formate tetrahydrate 5928-81-4  
 5929-01-1 5949-29-1, Citric acid monohydrate 5970-45-6, Zinc  
 acetate dihydrate 5971-93-7 5978-44-9 6011-38-7 6108-17-4,  
 Lithium acetate dihydrate 6131-90-4, Sodium acetate trihydrate  
 6138-53-0 6138-60-9 6153-39-5, Orcinol monohydrate 6163-66-2,  
 Di-tert-butyl ether 6164-85-8 6211-23-0 6225-10-1,  
 N-Methylpentanamide 6335-41-7, 4-Methoxyisonitrosoacetanilide  
 6335-42-8, 2-Methoxyisonitrosoacetanilide 6381-59-5 6531-38-0,  
 1,4-Piperazinediethanamine 6531-45-9, Lithium propionate  
 6600-40-4, L-Norvaline 6845-92-7, Diglycine nitrate 7154-79-2,  
 2,2,3,3-Tetramethylpentane 7289-52-3 7291-30-7 7341-63-1,  
 N-Allyl-N'-phenylthiourea 7346-41-0, 2-Chloroadamantane  
 7434-35-7, Perdeuterated triglycine sulfate 7782-40-3, Diamond,  
 properties

(thermodn. properties of)

IT 7782-42-5, Graphite, properties 9002-85-1, Polyvinylidene chloride  
 9002-86-2, Polyvinyl chloride 9002-88-4, Polyethylene 9002-89-5,  
 Polyvinyl alcohol 9003-17-2 9003-27-4, Polyisobutylene  
 9003-53-6, Polystyrene 9004-70-0, Cellulose nitrate 9011-14-7,  
 Poly(methyl methacrylate) 9043-05-4 10051-96-4, Trisarcosine  
 calcium chloride 10323-20-3, D-Arabinose 10368-91-9  
 10500-57-9, 5,6,7,8-Tetrahydroquinoline 11077-12-6, Azaferrocene  
 11077-24-0, Ferrocenium hexafluorophosphate 11078-19-6,  
 Bis(benzene)chromium chloride 11105-79-6 12070-79-0 12078-15-8  
 12078-16-9 12079-65-1, Cymantrene 12082-08-5, Benzene chromium  
 tricarbonyl 12082-87-0, Ferrocene-d10 12087-59-1,  
 Bis(toluene)chromium iodide 12089-29-1, Bis(benzene)chromium  
 iodide 12099-17-1, Bis(biphenyl)chromium iodide 12121-86-7  
 12148-59-3, Bis(mesitylene)chromium iodide 12156-67-1 12176-31-7  
 12257-73-7, Bis(ethylbenzene)chromium iodide 13146-23-1,  
 Copper phenylacetylenide 13373-97-2, 1-Eicosanethiol 13475-82-6,  
 2,2,4,6,6-Pentamethylheptane 13509-52-9, 1,3,6-Trimethyluracil  
 13963-57-0, Aluminum acetylacetonate 14024-18-1, Iron(III)  
 acetylacetonate 14024-63-6, Zinc acetylacetonate 14167-59-0,  
 Tetratriacontane 14240-75-6, Tetraethylammonium tetrachloroferrate  
 14618-78-1, 1,1-Dimethoxy-3-cyanopropane 14637-34-4 14690-98-3,  
 Copper (II) formate tetradeuterate 14722-82-8,  
 2-Chloroisonitrosoacetanilide 14879-21-1 14879-23-3 14901-07-6  
 14965-49-2, Methylammonium iodide 15649-95-3, Tetramethylammonium  
 tetrachloroferrate 15721-10-5, p-Methacryloyloxybenzoic acid  
 15844-05-0, Homocubane-4-carboxylic acid 16093-77-9 16093-78-0  
 16577-51-8, Lithium hexanoate 16594-83-5 16647-05-5 16649-52-8  
 16674-78-5, Magnesium diacetate tetrahydrate 16674-79-6, Strontium  
 dicalcium propionate 16761-13-0, Lithium heptanoate 16825-16-4,  
 Phytone 16986-24-6, m-Carborane 17082-12-1, trans-Azobenzene  
 17115-98-9, Barium dicalcium propionate 17122-74-6,

4-Ethoxyisonitrosoacetanilide 17203-66-6, Lead dicalcium  
 propionate 17356-96-6 17501-44-9, Zirconium acetylacetonate  
 18001-46-2 18030-61-0, p-Trichlorosilylbiphenyl 18254-57-4,  
 1,1-Dicyclohexyldodecane 18343-40-3, Hexaphenylmelamine  
 18616-15-4 18993-50-5 18993-51-6 18993-52-7 18993-53-8  
 19032-64-5 19049-40-2, Beryllium oxyacetate 19261-73-5  
 19269-28-4, 3-Methylhexanal 19288-59-6, Phenylaminoethyl  
 methacrylate 19353-21-0, 3,4-Dimethylpentanal 19361-62-7,  
 Styrene-d8 19455-20-0, Potassium 2-methylpropanoate 19479-83-5  
 20030-30-2 20267-19-0, 2-Hydroxyethyl pivalate 20267-21-4  
 20321-02-2, Hydrazinium hydrogen oxalate 21279-19-6,  
 Tetraethylammonium tetrabromoferrate 21303-03-7, Lithium butyrate  
 21482-12-2, Pentapropylene glycol 21679-31-2, Chromium  
 acetylacetonate 22428-30-4 22808-06-6, 2,2,5,5-Tetramethylhex-3-  
 ene 23014-56-4, 1,1,10,10-Tetramethylcyclooctadecane 23014-57-5  
 23307-02-0 23358-17-0 23672-37-9 23672-38-0 24028-46-4  
 24800-44-0, Tripropylene glycol 24888-58-2 24936-97-8  
 24968-12-5, Poly(butylene terephthalate) 24979-97-3,  
 Polytetrahydrofuran 24991-43-3, Butadiene-propylene copolymer  
 25014-31-7, Poly(.alpha.-methylstyrene 25036-32-2,  
 Polyvinyltrimethylsilane 25038-54-4, Poly[imino(1-oxo-1,6-  
 hexanediyl)], properties 25067-06-5, 1-Polyhexene 25067-58-7,  
 Polyacetylene 25067-64-5, Poly-1,3-dioxolane 25068-01-3,  
 Ethylene-butadiene copolymer 25085-53-4 25087-26-7,  
 Polymethacrylic acid 25214-70-4 25248-42-4, Poly[oxy(1-oxo-1,6-  
 hexanediyl)] 25265-71-8, Dipropylene glycol 25322-68-3  
 25456-55-7 25657-08-3, Tetrapropylene glycol 25686-28-6  
 25734-27-4, Poly[imino(1-oxo-1,2-ethanediyl)] 25853-28-5  
 25926-96-9 25926-99-2 25959-51-7 26202-08-4, Polyglycolide  
 26227-73-6 26692-50-2 26715-68-4 26744-16-1,  
 Polyvinyltrimethylphenylsilane 26745-88-0, Poly(hexamethylene  
 sebacate) 26760-54-3 26762-10-7, Poly(hexamethylene sebacate)  
 27426-98-8 27613-96-3 27732-42-9, Polystyrene-d8 27974-49-8,  
 .beta.-Selenodiglycol 28182-81-2 28183-09-7 28323-47-9,  
 Poly(diethylsiloxane) 28500-27-8 28576-60-5 28702-26-3  
 28702-43-4, Poly(1-pentene-1,5-diyl) 28702-45-6,  
 Poly(1-octene-1,8-diyl) 28726-71-8 29171-20-8 29412-62-2  
 29415-95-0, Manxane 29743-08-6 29743-10-0 29743-11-1  
 30209-80-4 31295-54-2 31401-34-0 31693-72-8 32761-36-7,  
 Azacymantrene 33440-88-9 33589-44-5 33734-55-3 33734-56-4  
 34028-37-0 34244-89-8 34244-90-1 34244-91-2 34244-92-3,  
 Thallium nonanoate 34375-89-8, 3-Methylpyrrolidine 34504-12-6  
 34507-12-5, Wurster's Blue perchlorate 34993-58-3 35165-78-7, •  
 Bis(m-xylene)chromium iodide 35280-78-5 35602-69-8, Cholesteryl  
 stearate 35705-97-6 35812-56-7 36376-18-8 36653-82-4,  
 1-Hexadecanol 37196-91-1 37541-72-3, Ammonium hydrogen oxalate  
 hemihydrate 37869-35-5, Hexamethyltrisilazane 38332-83-1  
 38423-62-0, 2-Ethoxyisonitrosoacetanilide 38454-35-2 38869-19-1



38974-20-8 39015-36-6 39060-95-2, 2,2'-Biindanyl 39470-17-2,  
 Biferrocenium triiodide 40317-63-3 40937-40-4, Methylammonium  
 hexachlorotellurate 41902-42-5, Tri-tert-Butylmethanol  
 42182-84-3 42182-87-6 42525-64-4 42572-91-8 47189-08-2  
 52709-84-9 52709-85-0 52794-80-6, Hexapropylene glycol  
 52910-78-8 53188-90-2 53261-61-3 55011-91-1, Thiourea nitrate  
 55671-71-1 56379-16-9 56544-26-4 56685-61-1 56993-57-8  
 57863-11-3 57863-12-4 57947-14-5 58675-48-2 58675-49-3  
 58675-50-6 59358-70-2 59358-71-3 59358-73-5 59454-35-2  
 59683-18-0 59789-07-0 59890-70-9 60046-87-9 60130-27-0,  
 Poly[(diphenylgermylene)-1,2-ethenediyl] 60435-70-3,  
 2-Methyl-1-heptanol 60970-45-8 61361-56-6 62155-50-4  
 62629-77-0 63287-55-8 63335-41-1 63424-48-6 63424-49-7  
 63441-99-6 64167-86-8  
 (thermodn. properties of)

L34 ANSWER 9 OF 14 HCA COPYRIGHT 2005 ACS on STN

80:59382 Bifunctional compounds in products of the liquid-phase  
 oxidation of n-**decane**. Syroezhko, A. M.; Potekhin, V. M.;  
 Proskuryakov, V. A. (Leningr. Tekhnol. Inst. im. Lensovet, Leningrad, USSR). Zhurnal Prikladnoi Khimii (Sankt-Peterburg, Russian Federation), 46(12), 2694-8 (Russian) 1973. CODEN: ZPKHAB. ISSN: 0044-4618.

AB Liq.-phase oxidn. of n-**decane** at 150.degree. gave  
 oxocarboxylic acids and .gamma.-alkylbutyrolactones in 1:1.75-2  
 ratio from the intermediate isomeric decanones via parallel  
 mechanisms; true esters constituted .apprx.7-10% of the product  
 mixt., which also included **lactides** and estolides.

IT 124-18-5  
 (oxidn. of, oxocarboxylic acids and lactones from)

RN 124-18-5 HCA

CN Decane (8CI, 9CI) (CA INDEX NAME)

Me-(CH<sub>2</sub>)<sub>8</sub>-Me

CC 23-16 (Aliphatic Compounds)

Section cross-reference(s): 22

ST oxidn **decane** oxocarboxylic acid; lactone oxidn  
**decane**

IT Alcohols, preparation

Esters, preparation

Ketones, preparation

(by liq.-phase oxidn. of **decane**)

IT Lactones

(from liq.-phase oxidn. of **decane**)

IT Carboxylic acids, preparation

(oxo-, from liq.-phase oxidn. of **decane**)

IT 64-19-7P, preparation 79-09-4P, preparation 104-50-7P  
 105-21-5P 107-92-6P, preparation 108-29-2P 109-52-4P,  
 preparation 123-76-2P 124-07-2P, preparation 142-62-1P,  
 preparation 624-16-8P 693-54-9P 820-29-1P 928-80-3P  
 1117-74-4P 1120-06-5P 1565-81-7P 2051-31-2P 3128-06-1P  
 3128-07-2P 4316-44-3P 5205-34-5P

(by liq.-phase oxidn. of **decane**)

IT **124-18-5**  
 (oxidn. of, oxocarboxylic acids and lactones from)

IT 111-14-8P  
 (prepn. of, by liq.-phase oxidn. of **decane**)

L34 ANSWER 10 OF 14 HCA COPYRIGHT 2005 ACS on STN

57:82780 Original Reference No. 57:16423c-i,16424a Syntheses of seven-membered ring compounds from furrural. II. Some reactions of pimelic acid derivatives. Suzuki, Kojiro (Univ. Osaka). Nippon Kagaku Zasshi, 82, 733-6 (Unavailable) 1961. CODEN: NPKZAZ. ISSN: 0369-5387.

AB .gamma.-Oxopimelic acid (I) (20 g.) shaken 2 days with 16 g. cinnamaldehyde (II) and 40 g. NaOH in 200 ml. H2O and 200 ml. MeOH, the soln. extd. with Et2O preceded by concn., the H2O layer acidified and again extd. with Et2O, the ext. concd., and the residue reduced over Pd-C in MeOH gave 9.2-11 g. Me .beta.-phenylpropyl-.gamma.-oxopimelate (III), b4 198-200.degree., n20D 1.5042. A mixt. of 5 parts H3PO4 and 3 parts P2O5 heated 2 hrs. at 100.degree., treated 2 hrs. with 1 part III at 55-60.degree., the product decompd. with ice water, and extd. with Et2O gave pale yellow viscous liquid (IV), b3 215-22.degree., n20D 1.5307. IV yielded III or iso-Pr .beta.-phenylpropyl-.gamma.-oxopimelate (V), b4 214-18.degree., through hydrolysis and subsequent esterification in MeOH or iso-PrOH, showing IV to be a lactone, not the expected 7-membered ring compd. .beta.-Phenylpropyl-.gamma.-oxopimelic acid (VI) treated with SOCl2 gave a viscous liquid, C18H23O3N, supposedly a **dilactone**, which was converted into an amide lactone, instead of the expected VI dimethylamide. Attempted ring closure of IIII with H2SO4 or HBr was unsuccessful. .alpha.-Ethoxycarbonyl-.gamma.,.gamma.-ethylenedioxycyclohexanone (VII) (Gardner, et al. (CA 50, 14691b)) in 50% NaOH kept 10 hrs. at room temp. and extd. continuously with Et2O gave from Et2O layer 70% .gamma.,.gamma.-ethylenedioxycyclohexanone-.alpha.-carboxylic acid (VIII), m. 143-6.degree., whose mother liquor **distsd.** gave .gamma.,.gamma.-ethylenedioxycyclohexanone (IX), m. 68-70.degree.. VII treated with NaOEt in abs. EtOH and subsequently with PhCHBrEt gave 61% .alpha.-ethoxycarbonyl-.alpha.-phenylpropyl-.gamma.,.gamma.-ethylenedioxycyclohexanone (X), b4 213-16.degree., n20D 1.5053. X shaken 10 hrs. in 60% EtOH contg. 5% NaOH at room temp. gave a monocarboxylic acid, which boiled 3 hrs. in HCl-EtOH and the

resulting oily product, b3.5 205-15.degree., treated with polyphosphoric acid (PPA) 3 hrs. at 70.degree. gave a **dilactone** (XI), C<sub>16</sub>H<sub>18</sub>O<sub>4</sub>, m. 81-2.degree.. X refluxed 3 hrs. in 55% H<sub>2</sub>SO<sub>4</sub> and extd. with Et<sub>2</sub>O after diln. with H<sub>2</sub>O gave from the ext. a dibasic acid (XII), C<sub>16</sub>H<sub>20</sub>O<sub>5</sub>, m. 100-1.degree., besides XI. X boiled with HBr resulted in the same products, while treated with HCl-EtOH X gave XII. X refluxed 1 hr. in EtOH contg. 10% KOH yielded .alpha.-phenylpropyl-.gamma.,.gamma.-ethylenedioxypimelic acid (XIII), m. 84-5.degree., converted to XII by boiling with 10% HCl. IX treated 24 hrs. at room temp. with cinnamaldehyde (XIV) (1:2.5 molar ratio) in 50% aq. MeOH contg. 5% NaOH deposited 65-70% .alpha.,.alpha.'-dicinnamylidene-.gamma.,.gamma.-ethylenedioxycyclohexanone (XV), m. 199-200.degree.. VII (1 mole) was treated with 1.1 moles XIV; the resulting ppt. gave from the ether-insol. part 50% XV and from the sol. part 10% .alpha.-cinnamylidene-.gamma.,.gamma.-ethylenedioxycyclohexanone-.alpha.'-carboxylic acid (XVI), m. 130.degree. (decompn.), besides 40% viscous acid, which reduced over Pd-C in MeOH and the resulting oil heated 1 hr. with PPA at 70.degree. gave XI. VII kept 10 hrs. in 5% NaOH and treated 40 hrs. with 1.1 moles XV in MeOH with shaking gave 40% XVI, besides a small amt. of XVI. XVI heated to decarboxylate yielded .alpha.-benzylidene-.gamma.,.gamma.-ethylenedioxycyclohexanone (XVII), m. 130-1.degree., which reduced in MeOH over Pd-C gave 2-phenylpropylcyclohexane-1,4-dione (XVIII), b3 185-8.degree., n<sub>20</sub>D 1.5366; disemicarbazone m. 230.degree.. XVIII heated 3 hrs. with 10 g. PPA at 150.degree. to obtain a cycloheptane compd. gave an oily product, analysis and the infrared spectra of which suggested that the expected compd. formed partly.

CC 28 (Alicyclic Compounds)

IT 4746-97-8, 1,4-Dioxaspiro[4.5]decan-8-one 5034-23-1,  
Cyclohexanone, 4-(2-methyl-1,3-dioxolan-2-yl)- 24133-20-8,  
5,9-Methanobenzocycloocten-11-one, dodecahydro-4a-hydroxy-10-propyl-  
90674-00-3, 1,4-Dioxaspiro[4.5]**decane**-7-carboxylic acid,  
8-oxo- 93998-80-2, Heptanedioic acid, 4-oxo-3-(3-phenylpropyl)-,  
dimethyl ester 93998-85-7, 1,3-Dioxolane-2,2-dipropionic acid,  
.alpha.-(3-phenylpropyl)- 94300-64-8, Heptanedioic acid,  
4-oxo-2-(3-phenylpropyl)- 94429-29-5, Heptanedioic acid,  
4,4-dihydroxy-2-(3-phenylpropyl)-, di-.gamma.-lactone 94752-84-8,  
1,4-Dioxaspiro[4.5]decan-8-one, 7-cinnamylidene- 94762-69-3,  
1,4-Dioxaspiro[4.5]**decane**-7-carboxylic acid,  
8-oxo-7-(3-phenylpropyl)-, ethyl ester 94824-13-2, 3-Heptenedioic  
acid, 4-hydroxy-3-(3-phenylpropyl)-, .gamma.-lactone, Me ester  
95156-89-1, 1,4-Dioxaspiro[4.5]**decane**-7-carboxylic acid,  
9-cinnamylidene-8-oxo- 95286-62-7, Heptanedioic acid,  
4-oxo-3-(3-phenylpropyl)-, diisopropyl ester 96667-87-7,  
1,4-Dioxaspiro[4.5]decan-8-one, 7,9-dicinnamylidene- 97376-66-4,  
1,4-Cyclohexanedione, (3-phenylpropyl)- 106571-87-3,  
1,4-Cyclohexanedione, (3-phenylpropyl)-, disemicarbazone

(prepn. of)

L34 ANSWER 11 OF 14 HCA COPYRIGHT 2005 ACS on STN

55:48695 Original Reference No. 55:9410g-i,9411a-e Syntheses by free-radical reactions. XII. Reactions of fluoroacyl radicals. Drysdale, J. J.; Coffman, Donald D. (E. I. du Pont de Nemours and Co., Wilmington, DE). Journal of the American Chemical Society, 82, 5111-15 (Unavailable) 1960. CODEN: JACSAT. ISSN: 0002-7863.

AB cf. CA 54, 15219f. Polyfluoroacyl chlorides and Ni(CO)<sub>4</sub> (Ia) formed F-contg. products derived from polyfluoroacyl radicals, polyfluoroalkyl radicals, and polyfluorocarbenes. The nature of the products was detd. by the medium and reaction conditions. C<sub>3</sub>F<sub>7</sub>COCl (115 g.) (I), 41 g. Ia and 300 g. PhCN stirred 72 hrs. at 25.degree. under anhyd. conditions, the mixt. filtered and the filtrate **distd.** gave 6 g. 5-hydrotetradecafluoro-4-oxo-5-octyl perfluorobutyrate, b<sub>18</sub> 64.degree., and 5 g. perfluoro-4-octene-4, 5-diol bis(perfluorobutyrate) (II), b<sub>18</sub> 89.degree.. A 51% conversion to II was obtained when the reaction time was increased to 12 days. II (600 g.) and 73 ml. MeOH gave 272 g. 5-hydrotetradecafluoro-5-hydroxy-4-octanone (III), b<sub>90</sub> 72.degree., n<sub>25D</sub> 1.4940. II was reduced with 10% Pd-C in HOAc to give 50% 4,5-dihydrotetradecafluoro-4,5-octanediol, b<sub>25</sub> 80.degree., m. 71-3.degree. (CHCl<sub>3</sub>). III, HOAc, and Bi triacetate gave perfluoro-4,5-octanedione (IV), b. 95.degree., identical with a sample prepd. by pyrolysis of II. IV was further characterized by the reaction with o-C<sub>6</sub>H<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub>, Ac<sub>2</sub>O, and EtOH to give 2,3-bis(perfluoropropyl)quinoxaline, b<sub>3</sub> 75.degree., n<sub>25D</sub> 1.4195. Further **distn.** of the residue gave a mixt. of HOAc and 3-hydrotridecafluoro-4,5-octanedione (V.), b. 108-10.degree.. Identity of V was confirmed by conversion to 2-(perfluoropropyl)-3-(1-hydrohexafluoropropyl)quinoxaline, m. 42-3.degree.. 5-Hydrooctafluorovaleryl chloride (VI), PhCN, and Ia stirred 14 days at 25.degree. under anhyd. conditions gave 1,6,10-trihydrohexadecafluoro-5-oxo-6-decyl 5-hydrooctafluorovalerate, b<sub>3-4</sub> 117.degree., and the enediol diester 1,10-dihydrohexadecafluoro-5-decene-5,6-diol bis(5-hydrooctafluorovalerate) (VIII), b<sub>3-4</sub> 124-9.degree., b<sub>20</sub> 167.degree., n<sub>25D</sub> 1.3255. The infrared spectrum suggested a trans structure. VII and MeOH gave 100% 1,6,10-trihydrohexadecafluoro-6-hydroxy-5-decanone, b<sub>50</sub> 74-6.degree., and Me 5-hydrooctafluorovalerate. Perfluoroglutaryl chloride (VIII) (100 g.), 62 g. Ia, and 20 g. PhCN stirred 3 days at room temp. under anhyd. conditions (CO slowly evolved, NiCl<sub>2</sub> pptd.) and the filtrate **distd.** gave 75 g. recovered VIII and 4 g. dodecafluoro-5,6-dihydroxy-trans-5-decene-1,10-dioic acid **dilactone**, m. 88-90.degree. (C<sub>6</sub>H<sub>6</sub>). I (46 g.), 34 g. Ia, and 176 g. C<sub>6</sub>H<sub>6</sub> heated 6 hrs. at 150.degree. with agitation in a stainless steel vessel gave on workup 18-20 g. perfluoropropylbenzene, b. 128.degree., n<sub>25D</sub> 1.3765. A mole ratio of

0.7:1 C<sub>6</sub>H<sub>6</sub>- I gave 10% bis(perfluoropropyl)benzene, b. 145.degree.. PhMe used in place of C<sub>6</sub>H<sub>6</sub> gave a mixt. of 2 isomeric perfluoropropyltoluenes in a 3:1 ratio, b100 87-9.degree., n<sub>25D</sub> 1.3905. Similarly, PhCF<sub>3</sub> and PhBr gave mixts. of isomeric perfluoropropyl-substituted benzenes; (10-hydroeicosafuorodecyl)benzene, b. 193.degree., m. 93.degree., was prepd. from C<sub>6</sub>H<sub>6</sub>, Ia, and 11-hydroeicosafuoroundecanoyl chloride (IX). VI and Ia heated 4 hrs. at 150.degree. in a pressure vessel gave 5.4% 5-hydrooctafluorovaleric acid and a complex mixt. sepd. by gas chromatography and contg. a 1,8-dihydrotetradecafluorooctene, 1,8-dihydrohexadecafluorooctane, and 1,9-dihydrohexadecafluoro-5-nonanone. I, Ia, and IX heated 16 hrs. at 150.degree. in stainless steel vessel gave 1,20-dihydrooctatriacontafluoro-10-eicosene, m. 89-91.degree., and a mixt., b. 82-96.degree., contg. 13-hydropentacosafuoro-3-tridecene, 13-hydropentacosafuoro-2-tridecene, and 1-hydroheptacosatridecane. Structures of these products, as well as all the others prepd., were supported or confirmed by F and proton magnetic resonance spectra and often by infrared spectra.

CC 10G (Organic Chemistry: Heterocyclic Compounds)  
 IT 307-99-3, Octane, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-hexadecafluoro-  
 378-98-3, Benzene, (heptafluoropropyl)- 423-66-5, Tridecane,  
 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13-  
 heptacosafuoro- 647-74-5, 4,5-Octanediol,  
 1,1,1,2,2,3,3,6,6,7,7,8,8,8-tetradecafluoro- 648-73-7,  
 4,5-Octanedione, 1,1,1,2,2,3,3,6,7,7,8,8,8-tridecafluoro-  
 678-37-5, 10-Eicosene, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,11,12,  
 12,13,13,14,14,15,15,16,16,17,17,18,18,19,19,20,20-  
 octatriacontafluoro- 678-91-1, 4-Octanone,  
 1,1,1,2,2,3,3,6,6,7,7,8,8,8-tetradecafluoro-5-hydroxy- 685-12-1,  
 5-Decene-5,6-diol, 1,1,2,2,3,3,4,4,7,7,8,8,9,9,10,10-hexadecafluoro-  
 , bis(2,2,3,3,4,4,5,5-octafluorovalerate) 755-64-6, 5-Nonanone,  
 1,1,2,2,3,3,4,4,6,6,7,7,8,8,9,9-hexadecafluoro- 1548-08-9,  
 4,5-Octanedione, tetradecafluoro- 1583-34-2, 5-Decanone,  
 1,1,2,2,3,3,4,4,7,7,8,8,9,9,10,10-hexadecafluoro-6-hydroxy-  
 1691-25-4, 4-Octanone, 1,1,1,2,2,3,3,6,6,7,7,8,8,8-tetradecafluoro-5-  
 hydroxy-, heptafluorobutyrate 1691-50-5, **Decane**,  
 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-eicosafuoro-1-phenyl-  
 1716-33-2, Quinoxaline, 2-(heptafluoropropyl)-3-(1,2,2,3,3,3-  
 hexafluoropropyl)- 2559-75-3, Quinoxaline, 2,3-  
 bis(heptafluoropropyl)- 2839-57-8, 3-Tridecene,  
 1,1,1,2,2,3,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13-  
 pentacosafuoro- 2926-91-2, 5-Decanone,  
 1,1,2,2,3,3,4,4,7,7,8,8,9,9,10,10-hexadecafluoro-6-hydroxy-,  
 2,2,3,3,4,4,5,5-octafluorovalerate 3932-48-7, 4-Octene-4,5-diol,  
 tetradecafluoro-, bis(heptafluorobutyrate) 29595-18-4, Benzene,  
 bis(heptafluoropropyl)- 109342-36-1, 2-Tridecene,  
 1,1,1,2,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13-

pentacosafuoro-  
(prepn. of)

L34 ANSWER 12 OF 14 HCA COPYRIGHT 2005 ACS on STN

53:67700 Original Reference No. 53:12279h-i,12280a-i,12281a Synthetic applications of activated metal catalysts. VI. Desulfurizations with Raney cobalt. Badger, G. M.; Kowanko, N.; Sasse, W. H. F. (Univ. Adelaide, S. Australia). Journal of the Chemical Society, Abstracts 440-4 (Unavailable) 1959. CODEN: JCSAAZ. ISSN: 0590-9791. OTHER SOURCES: CASREACT 53:67700.

AB cf. C.A. 52, 9068h. Raney Co (I) was used to desulfurize dibenzothiophene (II) and a no. of acylthiophenes, thiophenecarboxylic acids, thiazoles, and thioamides. In general it is less effective than Raney Ni, but some differences were noted. W-7 I was prepd. from Co-Al alloy (30% Co, 70% Al) by the same method used for W-7 Raney Ni [Org. Syntheses Collective Vol. III, 179(1955)]. The more active "Aller" I was prepd. at 15-20.degree.. 2-Acetylthiophene (III) (30 g.), W-7 I (from 125 g. alloy), and 200 cc. MeOH refluxed 5 hrs., the filtrate and MeOH exts. combined, MeOH removed, and the residue **distd.** gave 3 fractions: (a) 2.77 g. 2-hexanone, b30 60.degree.; (b) 26.3 g. unchanged material, b20 102.degree.; and (c) an oil, b0.5 80-90.degree. which when redistd. gave 10 mg. **dodecane-2,11-dione** (IV), m. 54-6.degree.. III (60 g.), W-7 I (from 250 g. alloy), and 250 cc. MeOH refluxed 24 hrs. and **distd.** gave the following fractions: (a) 1 g. nonketonic forerun, b22 100.degree.; (b) 50.75 g. unchanged III, and (c) 0.996 g. oil, b0.03 90-120.degree.; and (d) a small amt. of solid. Fraction c was extd. with ligroine, and chromatographed to give IV. The ligroine-insol. portion was identified as a compd., m. 88.5-9.0.degree. whose spectra suggested a COC:C system, and a CH<sub>2</sub> absorption at 6.99 .mu.. 2-Benzoylthiophene (V) (30 g.), W-7 I (from 125 g. alloy), and 200 cc. MeOH refluxed 5 hrs. and **distd.** gave (a) 1.83 g. valerophenone (VI), b0.05 80.degree.; (b) 24.75 g. unchanged V, b0.05 100-2.degree.; and (c) a residue from which 1,8-dibenzoyloctane (VII) could not be obtained. A repeat of this run using "Aller" I gave 2.2 g. VI, 25.5 g. unchanged V, and 0.5 g. crude VII which on crystn. gave 30 mg. pure VII, m. 92-3.degree.. 3-Acetylthianaphthene (VIII) (30 g.), W-7 I (from 125 g. alloy), and 200 cc. MeOH refluxed 5 hrs., and **distn.** gave a mixt. of 4.44 g. from which 1.4 g. 3-phenylbutan-2-one, b24 110-12.degree. was obtained; 2,4-dinitrophenylhydrazon m. 171-2.degree.. VIII (27.2 g.) and a small intractable residue were recovered. Thiophene-2-carboxylic acid (5 g.), W-7 I (from 65 g. alloy), and 10% aq. Na<sub>2</sub>CO<sub>3</sub> heated 2 hrs. at 80-90.degree., the catalyst removed, and washed with hot Na<sub>2</sub>CO<sub>3</sub> soln. followed by acidification gave 3.75 g. unchanged material and valeric acid (isolated as the p-bromobenzylisothiuronium salt, m. 162.degree.).

.gamma.-2-Thienylbutyric acid (IX) (8 g.) similarly treated 1.75 hrs. with W-7 I and 10% Na<sub>2</sub>CO<sub>3</sub> gave 2.57 g. octanoic acid (X), b<sub>0.05</sub> 72-3.degree., 4.90 g. unchanged IX, and 0.2 g. of residue which gave about 8 mg. impure hexadecane-1,16-dicarboxylic acid (XI). IX (30 g.), W-7 I, and aq. Na<sub>2</sub>CO<sub>3</sub> heated 5 hrs. gave 7.93 g. X, 18.9 g. IX, and 1.2 g. residue contg. some XI. .beta.-2-Thenoylpropionic acid (7 g.), W-7 I, and aq. Na<sub>2</sub>CO<sub>3</sub> refluxed 5 hrs., the catalyst extd. with dil. Na<sub>2</sub>CO<sub>3</sub>, the combined filtrates acidified and cooled yielded 0.27 g. 4,13-dioxohexadecanedioic acid, m. 152-3.degree.. Conc'n. of the mother liquors gave 1.415 g. unchanged material and the liquors extd. with Et<sub>2</sub>O, evapd., and the product **distd** gave 4 fractions: (a) 0.89 g. 4-hydroxyoctanolactone, b<sub>22</sub> 114-18.degree., n<sub>D</sub> 1.4456; (b) 0.62 g., b<sub>22</sub> 152-66.degree.; (c) 0.54 g., b<sub>22</sub> 180.degree.; and (d) 0.5 g. residue. Recrystn. of a and b gave 4-oxooctanoic acid, m. 50-2.degree., and the residue yielded 3.7 mg. 4,13-dihydroxyhexadecane-1,16-dioic acid **dilactone**, m. 76-8.degree.. 2-Amino-4-phenylthiazole (5 g.), W-7 I (from 65 g. alloy), and 250 cc. MeOH refluxed 4 hrs. under N, and the gases passed into dil. HCl gave 0.15 g. NH<sub>4</sub>Cl. The mixt. furnished 4.4 g. unchanged material and 0.55 g. acetophenone, identified as the dinitrophenylhydrazone. 2-Mercaptobenzothiazole (10 g.) and W-7 I (from 65 g. alloy) in 250 cc. MeOH refluxed 4.5 hrs., the catalyst removed, washed with MeOH, and the combined filtrates acidified and steam **distd**. gave 3 g. unchanged material. The liquors treated with 9 g. p-MeC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>Cl and aq. alkali and the mixt. steam **distd**. gave 2.74 g. benzothiazole but amines could not be detected. A similar attempt to desulfurize 10 g. benzothiazole gave 6.08 g. unchanged material and a tar. II (5 g.), W-7 I (from 40 g. alloy), and 200 cc. alc. refluxed 14 hrs., the filtrate evapd. and the residue extd. with C<sub>6</sub>H<sub>6</sub>, solvent evapd., and the product crystd. gave after chromatography 1.8 g. unchanged II, m. 98-9.degree.; picrate m. 123-4.degree.. Evapn. of the liquors gave 1.2 g. Ph<sub>2</sub>, m. 69-70.degree.. Phenanthridinethione (1 g.), 10 cc. HCONMe<sub>2</sub>, 10 cc. alc., and W-7 I (from 10 g. alloy), refluxed 1.5 hrs., the catalyst removed, and the combined filtrates evapd. gave 0.61 g. phenanthridine, m. 105-6.degree.. Similar desulfurization in C<sub>5</sub>H<sub>5</sub>N gave less pure material. 2-Mercaptoquinoline (XII) (3 g.), W-7 I (from 30 g. alloy), and 60 cc. MeOH refluxed 5 hrs. gave 0.026 g. 2,2'-diquinolyl (XIII), m. 193-4.degree. and 4.10 g. quinoline; picrate m. 203.degree.. The mixed catalyst and brown solid extd. with hot HCONMe<sub>2</sub> 12 hrs. gave 0.455 g. tris(2-mercaptoquinoline)cobalt. The HCONMe<sub>2</sub> exts. dild. and the solid chromatographed in C<sub>6</sub>H<sub>6</sub> on Al<sub>2</sub>O<sub>3</sub> gave 0.295 g. XIII, m. 193.degree. (red complex with Cu<sup>+</sup>), and 0.045 g. di-2-quinolyl sulfide (XIV), m. 188.degree. (ligroine). The complex, not affected by dil. HCl, was heated with concd. HCl at 140-60.degree., poured into concd. NaOH, and extd. with Et<sub>2</sub>O to give XII and XIV. Acridinethione (3 g.), 30 cc. HCONMe<sub>2</sub>, 30 cc. alc., and W-7 I (from 30 g. alloy) refluxed 13

hrs., the catalyst sepd., the filtrates evapd., and the residue extd. with refluxing 0.5N NaOH gave 0.92 g. starting material. The alkali-insol. portion when continuously extd. with ligroine for 2 hrs. gave acridine. The ligroine-insol. fraction (0.85 g.) chromatographed on Al<sub>2</sub>O<sub>3</sub> in PhCl gave 0.43 g. 9,9'-diacridyl, m. 393.degree.. Imidazolidinethione (10 g.), W-7 I (from 125 g. alloy), and 250 cc. MeOH refluxed 5 hrs. gave 302 g. unchanged material, m. 197-8.degree.. Evapn. of the mother liquors gave (CH<sub>2</sub>NH<sub>2</sub>)<sub>2</sub>. The residue gave 1.61 g. unchanged material and 3.28 g. of a viscous oil, b0.01 190.degree., which was triturated with alc. to give 2.68 g. N,N-diformylethylenediamine, m. 109-10.degree. (alc.-EtOAc).

CC 10G (Organic Chemistry: Heterocyclic Compounds)

L34 ANSWER 13 OF 14 HCA COPYRIGHT 2005 ACS on STN

50:77792 Original Reference No. 50:14691b-i 3,7-Dicarbethoxy-5-hydroxytropolone. A convenient synthesis of pimelic acid. Gardner, Pete D.; Rand, Leon; Haynes, G. Rufus (Univ. of Texas, Austin). Journal of the American Chemical Society, 78, 3425-7 (Unavailable) 1956. CODEN: JACSAT. ISSN: 0002-7863. OTHER SOURCES: CASREACT 50:77792.

AB Furfural (135 g.), 152 g. CH<sub>2</sub>(CO<sub>2</sub>H)<sub>2</sub>, 250 cc. pyridine, and 3 cc. piperidine heated 2.5 hrs. on the steam bath, refluxed 45 min., poured into 400 g. H<sub>2</sub>SO<sub>4</sub> and 2 kg. ice, and filtered, the filter cake washed with cold H<sub>2</sub>O and dissolved as rapidly as possible in 600 cc. hot MeOH, and the soln. dild. with 900 cc. hot H<sub>2</sub>O and cooled 24 hrs. to 0.degree. gave 166 g. furylacrylic acid (I), m. 140-1.degree. (all m.ps. are cor.). I (382 g.) gave by the method of Singleton (C.A. 42, 5048h) 476 g. OC[(CH<sub>2</sub>)<sub>2</sub>CO<sub>2</sub>Et]<sub>2</sub> (II), b26 180-90.degree. [2,4-dinitrophenylhydrazone, m. 82-3.degree. (from EtOH)], 55.1 g. mixt., b. 190-220.degree., and 45.5 g. **distillate**, b26 220-35.degree., which crystd. and gave 33.0 g. HO<sub>2</sub>C(CH<sub>2</sub>)<sub>2</sub>CO(CH<sub>2</sub>)<sub>2</sub>CO<sub>2</sub>Et, m. 71-2.degree.. I treated similarly with MeOH gave 60% OC[(CH<sub>2</sub>)<sub>2</sub>CO<sub>2</sub>Me]<sub>2</sub>, m. 51-2.degree., and 10% HO<sub>2</sub>C(CH<sub>2</sub>)<sub>2</sub>CO(CH<sub>2</sub>)<sub>2</sub>CO<sub>2</sub>Me, m. 62-3.degree.; the di-Me ester gave a 2,4-dinitrophenylhydrazone, m. 67-8.degree. (from MeOH). In one run about 10% yield of .gamma.-oxopimelic acid **dilactone** (2,2'-spirotetrahydropyran-5-one (III)), m. 63-4.degree., was obtained, I (53.8 g.), 230 cc. 95% N(CH<sub>2</sub>CH<sub>2</sub>OH)<sub>3</sub>, 60 g. 85% KOH, and 37 cc. 85% N<sub>2</sub>H<sub>4</sub>.H<sub>2</sub>O refluxed 2.5 hrs., heated without condenser to 195.degree., refluxed 2 hrs., cooled, acidified with 450 cc. HCl (d. 1.18), and extd. 16 hrs. with Et<sub>2</sub>O, the ext. evapd., and the residue recrystd. from concd. HCl gave 37.2 g. CH<sub>2</sub>[(CH<sub>2</sub>)<sub>2</sub>CO<sub>2</sub>H]<sub>2</sub> (IV), m. 103.5-105.degree.. III gave in a similar run 94% IV. In the prepn. of 3,7-dicarbethoxytropolone by the method of Cook, et al. (C.A. 49, 3038a), was also obtained 3% 1-carboxy-1-hydroxy-2,6-dicarbethoxycyclohexane, m. 132.degree.. II (476 g.), 1.5 l. C<sub>6</sub>H<sub>6</sub>, 134 g. (CH<sub>2</sub>OH)<sub>2</sub>, and 2 g. p-MeC<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>H refluxed 15 hrs.



**azeotropically** (40 cc. aq. layer collected), the mixt. cooled, treated with 0.5 g. Na in 15 cc. EtOH, swirled 1 min., and dild. with cold H<sub>2</sub>O, and the C<sub>6</sub>H<sub>6</sub> layer worked up yielded 129.7 g. unchanged II, b0.4 124.degree., nD<sub>25</sub> 1.4383, and 169.7 g. di-Et 4,4-ethylenedioxypimelate (IVa), b0.3 134.degree., nD<sub>25</sub> 1.4463. IVa (27.4 g.) in 50 cc. dry Et<sub>2</sub>O added to dry NaOEt from 2.3 g. Na, the mixt. shaken vigorously, stirred, kept 48 hrs. in the dark, cooled to 0.degree., and acidified with 11 cc. concd. HCl in 50 cc. H<sub>2</sub>O, and the Et<sub>2</sub>O layer worked up gave 12.4 g. 2-carbethoxy-4,4-ethylenedioxycyclohexanone (V), b0.5 114.degree., nD<sub>25</sub> 1.4846, a small intermediate fraction, and 8.1 g. unchanged IVa, b0.7 127.degree., nD<sub>25</sub> 1.4486. (CO<sub>2</sub>Et)<sub>2</sub> (28.0 g.) and 49.2 g. IVa added to dry NaOEt from 8.72 g. Na in 150 cc. dry Et<sub>2</sub>O, the mixt. refluxed 1 hr., kept 3 hrs. in a bath with the removal of EtOH and Et<sub>2</sub>O, the residual dark mass cooled, dissolved in H<sub>2</sub>O, acidified with cold, dil. HCl, and extd. with Et<sub>2</sub>O, the ext. washed with satd. aq. Na<sub>2</sub>CO<sub>3</sub> and H<sub>2</sub>O, and treated with 8N NaOH, the yellow solid filtered by suction, dissolved in H<sub>2</sub>O, and acidified, and the ppt. recrystd. several times from EtOH gave 10.5 g. 3,7-dicarbethoxy-5,5-ethylenedioxy-1,2-cycloheptanedione (VI), colorless needles, m. 122.5-24.degree.; after several months a sample m. 102-15.degree.. VI (0.10 g.) and 0.14 g. PhNHNH<sub>2</sub> refluxed 20 min. in 5 cc. EtOH gave the dipyrazolone deriv., pale yellow solid, m. 237-50.degree. (with gradual decompn.) (from EtOH). VI (1 g.) in 10 cc. 25% aq. H<sub>2</sub>SO<sub>4</sub> refluxed 2 hrs., cooled, dild. with 20 cc. H<sub>2</sub>O, and extd. with CHCl<sub>3</sub>, and the ext. washed, dried, and dild. with Et<sub>2</sub>O yielded 0.21 g. 3,7-dicarbethoxy-1,2,5-cycloheptanetrione, m. 128-8.5.degree. (from EtOH). Br (0.56 g.) added dropwise with stirring to 1.00 g. VI in 15 cc. AcOH at 100, the mixt. warmed to 25.degree. and evapd. in vacuo, and the yellow residue crystd. from EtOH yielded 0.708 g. 3,7-dicarbethoxy-5-hydroxytropolone, yellow solid, m. 168-70.degree. (decompn.) (from EtOH); it gave a yellow color in aq. NaHCO<sub>3</sub> and a black color with alc. FeCl<sub>3</sub>; it yielded a solid, turquoise Cu salt from aq. CuSO<sub>4</sub>.

CC 10 (Organic Chemistry)

IT 111-16-0, Pimelic acid 539-47-9, 2-Furanacrylic acid 3505-67-7, Heptanedioic acid, 4,4-dihydroxy-, di-.gamma.-lactone 14160-65-7, 1,4-Dioxaspiro[4.5]**decane**-7-carboxylic acid, 8-oxo-, ethyl ester 17448-96-3, Malonic acid, furfurylidene-, diethyl ester 19719-88-1, 1,3-Dioxolane-2,2-dipropionic acid, diethyl ester 94251-37-3, 1,4-Dioxaspiro[4.6]undecane-7,10-dicarboxylic acid, 8,9-dioxo-, diethyl ester (prepn. of)

L34 ANSWER 14 OF 14 HCA COPYRIGHT 2005 ACS on STN

49:19860 Original Reference No. 49:3858b-i,3859a-g The diene synthesis. XL. Diene syntheses with 1,3,5-cycloheptatriene. Alder, Kurt; Jacobs, Glinter (Univ. Cologne, Germany). Chemische Berichte, 86,

1528-39 (Unavailable) 1953. CODEN: CHBEAM. ISSN: 0009-2940.

GI For diagram(s), see printed CA Issue.

AB Because in a diene synthesis trienes behave like dienes, the diene synthesis of 1,3,5-cycloheptatriene (I) is reinvestigated. I and maleic anhydride (II) give an adduct which, on hydrogenation, gives a di- (III) or tetrahydro deriv. (IV) [putative 3,6-ethano-7-methylhexahydrophthalic anhydride IVa], depending upon the exptl. conditions. III is quite stable toward Br and KMnO<sub>4</sub>. IV is not identical with the compd. obtained on condensation of 1,3-cycloheptadiene with II followed by hydrogenation. They are not stereoisomers, but they are structurally different. These observations suggest that in the diene synthesis I undergoes a rearrangement by an "intracyclic diene synthesis" into norcaradiene (V). When 10 g. I is refluxed 5 hrs. with an excess of II in xylene and the xylene is **distd.** off in vacuo endo-cis-3,6-endocyclopropylene-**DELTA**.4-tetrahydrophthalic anhydride (VI), needles, m. 101.degree., is obtained. Heating 900 cc. of a soln. (VII) of I and V in C<sub>6</sub>H<sub>6</sub>, prep'd. according to Meerwein (cf. van de Vloed, Thesis, Marburg, 1946), with 25 g. II 12 hrs. at 140-50.degree. and evapg. the decolorized soln. on a water bath give VI. Boiling 1 g. VI with 10% Na<sub>2</sub>CO<sub>3</sub> and acidifying with dil. HCl give the acid (VIII), m. 173.degree. (di-Me ester (VIIIa), prep'd. by refluxing 1 g. VI in 10 cc. MeOH and 10 cc. C<sub>6</sub>H<sub>6</sub> 4 hrs. with 1 cc. concd. H<sub>2</sub>SO<sub>4</sub>, fine needles, m. 70.degree.). Hydrogenation of 5 g. VI in 20 cc. AcOH with PtO<sub>2</sub> gives III, scales, m. 140.degree.. Treating 0.5 g. VIII in 100 cc. H<sub>2</sub>O with Br gives the bromo lactone acid (IX), needles, m. 185.degree., which, treated with 20% KOH on a water bath and acidified, gives the OH lactone acid (X), m. 279-82.degree.. Boiling X 1 hr. with Ac<sub>2</sub>O gives the **dilactone** (XI), thick columns, m. 291-3.degree. (decompn.). Adding dropwise a 5% KMnO<sub>4</sub> soln. to 5 g. VI in Na<sub>2</sub>CO<sub>3</sub> soln. at 20.degree. until the supernatant soln. is slightly red, simultaneously passing CO<sub>2</sub> into the mixt., heating it to boiling, acidifying the filtered soln. with HCl, evapg. to dryness, and extg. the residue with EtOAc give 4,5-dioxo-3,6-endocyclopropylenehexahydrophthalic acid (XII), rosettes of needles, m. 168-9.degree., which, refluxed 12 hrs. with Ac<sub>2</sub>O and evapd. in vacuo, gives the anhydride, yellow needles, m. 236-40.degree. [di-Me ester (XIII), prep'd. by refluxing 2 g. XII in 20 cc. MeOH and 20 cc. C<sub>6</sub>H<sub>6</sub> 6 hrs. with 2 cc. concd. H<sub>2</sub>SO<sub>4</sub>, thin yellow platelets, m. 150.degree.]. Warming 2.6 g. XIII and 1 g. o-C<sub>6</sub>H<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub> in 60 cc. C<sub>6</sub>H<sub>6</sub> and 6 cc. AcOH 10 min. on a water bath gives the quinoxaline deriv., small rods, m. 216-18.degree.. Adding 5 cc. 30% H<sub>2</sub>O<sub>2</sub> to 2 g. XII in 100 cc. 5% NaOH with cooling, refluxing the mixt. 0.5 hr., acidifying with dil. HCl, evapg. to dryness, extg. the residue with Ac<sub>2</sub>O, and refluxing the ext. 2 hrs. give 1.2 g. norcarantetracarboxylic acid dianhydride (XIV), m. 206-7.degree.. Adding a 15% NaMnO<sub>4</sub> soln. to 15 g. VI in 250 cc. H<sub>2</sub>O and an excess

of  $\text{Na}_2\text{CO}_3$  at 0-50.degree. with stirring and passing  $\text{CO}_2$  through the mixt., destroying the excess  $\text{NaMnO}_4$  with a little MeOH, evapg. the filtered and acidified soln. in vacuo to dryness, and extg. the residue with Ac<sub>2</sub>O give 8 g. XIV which, converted into the acid and methylated with  $\text{CH}_2\text{N}_2$ , gives the tetra-Me ester, m. 107-8.degree.. Adding at 0.degree. 5%  $\text{KMnO}_4$  soln. to 5 g. VII in 250 cc. H<sub>2</sub>O and 40 cc. dil. H<sub>2</sub>SO<sub>4</sub>, concg. the filtered soln. to 1/3 its vol., and extg. with EtOAc give the "O5 compd." (XV), crystals from EtOAc, m. 243-6.degree. which is unreactive toward  $\text{CH}_2\text{N}_2$ ,  $\text{Na}_2\text{CO}_3$ , and 5%  $\text{KMnO}_4$  in the cold. Adding a 15%  $\text{NaMnO}_4$  soln. to 1 g. XV in 100 cc. dil.  $\text{Na}_2\text{CO}_3$  and 150 cc. H<sub>2</sub>O with stirring and passing  $\text{CO}_2$  through the soln., evapg. the filtered and acidified soln. to dryness, extg. the residue with MeOH, and treating the ext. with  $\text{CH}_2\text{N}_2$  give 0.1 g. XIII. Refluxing 2 g. I, prepd. according to Kohler (C.A. 33, 6256.7), with a small excess of fumaroyl chloride in C<sub>6</sub>H<sub>6</sub> 3 hrs., **distg.** off the C<sub>6</sub>H<sub>6</sub>, pouring the residue into abs. MeOH, and fractionally **distg.** the mixt. give di-Me trans-3,6-endocyclopropylene-.DELTA.4-tetrahydrophthalate (XVI), fine needles, m. 49-50.degree., which is also obtained when 900 cc. VII is refluxed 12 hrs. with 40 cc. fumaroyl chloride. Heating 1 g. VIII 5 hrs. at 180-200.degree. with concd. HCl, evapg. the soln., and treating the residue in MeOH with  $\text{CH}_2\text{N}_2$  give 0.1 g. XVI. Treating 1 g. VIIIA 5 hrs. with 1 g. Na in 15 cc. MeOH, adding 50 cc. H<sub>2</sub>O, boiling the mixt. 0.5 hr., **distg.** off the MeOH, dilg. with 200 cc. H<sub>2</sub>O, acidifying the washed (ether) soln. with HCl, and treating the residue of the evapd. soln. in MeOH with  $\text{CH}_2\text{N}_2$  give XVI also. Hydrogenating 1 g. VIIIA in 50 cc. EtOAc in the presence of Raney Ni 3-4 hrs., sapong. the residue of the evapd. soln. with 20% KOH-MeOH, and acidifying the soln. with HCl give the satd. acid of III, platelets, m. 220.degree.. Heating 900 cc. VII with 40 cc. (.tpltbond.CC<sub>2</sub>OEt)<sub>2</sub> 36 hrs. at 160.degree., **distg.** off the C<sub>6</sub>H<sub>6</sub>, and **distg.** the residue give di-Me 3,6-endocyclopropylene .DELTA.1,4-dihydrophthalate (XVII), viscous oil, b<sub>0.02</sub> 95-100.degree. which, refluxed 2 hrs. with 20% KOH, gives 10-13 g. free acid, fine needles, m. 143-4.degree.. Shaking 5 g. XVII in 100 cc. EtOAc in the presence of Raney Ni with H and sapong. the ester give 3,6-endoecyclopropylene-.DELTA.1-tetrahydrophthalic acid (XVIII), needles, m. 173-4.degree., which is not identical with VIII. Catalytic hydrogenation of 5 g. XVII 5 hrs. at 150 atm. and 100.degree. and sapon. of the ester give the free acid of III. Heating 5 g. XVII 1 hr. at 240.degree. and **distg.** the product give o-C<sub>6</sub>H<sub>4</sub>(CO<sub>2</sub>Me)<sub>2</sub>. Adding a 15%  $\text{NaMnO}_4$  soln. to 3.5 g. XVII in dil.  $\text{Na}_2\text{CO}_3$  at 80.degree. while passing  $\text{CO}_2$  into the soln., destroying the excess  $\text{NaMnO}_4$ , evapg. the filtered and acidified soln., extg. the residue with Me<sub>2</sub>CO, and refluxing the residue of the evapd. ext. with AcCl give 1,2-cyclopropanedicarboxylic anhydride, needles, m. 60.degree.. The steric configuration of these compds. is discussed.

CC 10 (Organic Chemistry)  
IT 1,5-Methano-1H-cycloprop[e]isobenzofuran-4-carboxylic acid, 7-bromo  
octahydro-3-oxo-  
11,13-Dioxapentacyclo[3.2.2.26,9.27,8.02,4]-tridecane-10,12-dione  
2,3,4,5-Norcaranetetra-carboxylic acid  
2,3,4,5-Norcaranetetra-carboxylic acid, tetramethyl ester  
2,3,4,5-Norcaranetetra-carboxylic dianhydride  
2,4-Norcaradiene, 3,4-trimethylene-  
2,9-Ethano-1H-cyclopropa[b]phenazine-10,11-dicarboxylic acid,  
1a,2,9,9a-tetrahydro-, dimethyl ester  
3,4-Trimethylenenorcaradiene-2,4-diene  
3,6-Endocyclopropylenephthalic acid, hexahydro-4,5-dioxo-  
3,6-Endocyclopropylenephthalic acid, .DELTA.1,4-dihydro-  
3,6-Endocyclopropylenephthalic acid, .DELTA.1,4-dihydro-, dimethyl  
ester  
3,6-Endocyclopropylenephthalic acid, .DELTA.4-tetrahydro-, dimethyl  
ester, cis-  
3,6-Endocyclopropylenephthalic acid, .DELTA.4-tetrahydro-, cis-  
3,6-Endocyclopropylenephthalic anhydride, hexahydro-4,5-dioxo-  
3,6-Endocyclopropylenephthalic anhydride, .DELTA.4-tetrahydro-,  
endo-cis-  
4,6-(Methanoxy-methano)-1H-cycloprop[f]isobenzofuran-1,3,7,9(3a-H)-  
tetrone, hexahydro-  
4,6-Ethano-1H-cycloprop[f]isobenzofuran-1,3(3aH)-dione, hexahydro-  
4,6-Ethano-1H-cycloprop[f]isobenzofuran-1,3,7,8(3aH)-tetrone,  
hexahydro-  
4,6-Etheno-1H-cycloprop[f]isobenzofuran-1,3-(3aH)-dione,  
4,4a,5,5a,6,6a-hexahydro-, cis-  
7,12,14-Trioxapentacyclo[3.3.2.26,10.28,9.02,4]tetradecane-11,13-  
dione  
7-Oxatricyclo[3.3.2.02,4]decane-9,10-dicarboxylic acid,  
6,8-dihydroxy-, di- $\gamma$ -lactone  
Cycloprop[f]indene, 1,1a,3,4,5,6a-hexahydro-  
Phthalic acid, 3,6-endo-cyclopropylene-.DELTA.1,4-dihydro-  
Phthalic acid, 3,6-endo-cyclopropylene-.DELTA.1,4-dihydro-, dimethyl  
ester  
Phthalic acid, 3,6-endo-cyclopropylene-.DELTA.4-tetrahydro-,  
dimethyl ester of cis-  
Phthalic acid, 3,6-endo-cyclopropylene-.DELTA.4-tetrahydro-,  
dimethyl ester of trans-  
Phthalic acid, 3,6-endo-cyclopropylene-.DELTA.4-tetrahydro-, cis-  
Phthalic acid, 4,5-dioxo-3,6-endo-cyclopropylenehexahydro-  
Phthalic anhydride, 3,6-endo-cyclopropylene-.DELTA.4-tetrahydro-,  
endo-cis-  
Phthalic anhydride, 4,5-dioxo-3,6-endo-cyclopropylenehexahydro-  
Tricyclo[3.2.2.02,4]non-6-ene-6,7-dicarboxylic acid  
Tricyclo[3.2.2.02,4]non-8-ene-6,7-dicarboxylic acid, dimethyl ester  
of cis- isomer

Tricyclo[3.2.2.02,4]non-8-ene-6,7-dicarboxylic acid, dimethyl ester of trans-isomer  
 Tricyclo[3.2.2.02,4]non-8-ene-6,7-dicarboxylic acid, cis-  
 Tricyclo[3.2.2.02,4]non-8-ene-6,7-dicarboxylic anhydride, cis-  
 Tricyclo[3.2.2.02,4]nonane-6,7-dicarboxylic acid  
 Tricyclo[3.2.2.02,4]nonane-6,7-dicarboxylic acid, 8,9-dihydroxy-, .gamma.-lactones  
 Tricyclo[3.2.2.02,4]nonane-6,7-dicarboxylic acid, 8,9-dioxo-  
 Tricyclo[3.2.2.02,4]nonane-6,7-dicarboxylic acid, 8,9-dioxo-, dimethyl ester  
 Tricyclo[3.2.2.02,4]nonane-6,7-dicarboxylic acid, 8-bromo-9-hydroxy-, .gamma.-lactone  
 Tricyclo[3.2.2.02,4]nonane-6,7-dicarboxylic anhydride, 8,9-dioxo-

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L35 ANSWER 1 OF 20 HCA COPYRIGHT 2005 ACS on STN

140:28777 Cleaning compositions containing dichloroethylene and alkoxy substituted perfluoro compounds having six carbon atoms. Doyel, Kyle; Bixenman, Michael (Kyzen Corporation, USA). U.S. Pat. Appl. Publ. US 2003228997 A1 20031211, 15 pp. (English). CODEN: USXXCO. APPLICATION: US 2002-164308 20020607.

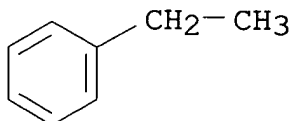
AB A cleaning compn. comprises dichloroethylene and one or more alkoxy-substituted perfluoro compds. that contain six carbon atoms and have the general formula R1-O-R2, where R1 is perfluorobutyl and R2 is Et, or R1 is perfluoropentyl and R2 is Me, and an additive selected from (a) a highly fluorinated compd. of the formula CaFbHcXd, where a is from 2 to 8, b is > a but < (2a+2), d is 0,1, or 2, c is .ltoreq. (2a+2-b-d), and X is O, N, halogen, or Si, (b) an enhancement agent selected from alcs., **esters**, ethers, **cyclic** ethers, ketones, alkanes, aroms., amines, siloxanes, terpenes, dibasic esters, glycol ethers, pyrrolidones, low or non-ozone depleting halogenated hydrocarbons, and (c) mixts. of (a) and (b). The highly fluorinated compds. retard flammability of the cleaning compn., and the enhancement agents improve the cleaning or solvating properties. The cleaning compns. are useful in a variety of solvating, vapor degreasing, photoresist stripping, adhesive removal, aerosol, cold cleaning, and solvent cleaning applications, including defluxing, dry-cleaning, degreasing, particle removal, metal and textile cleaning. Thus, a nonflammable cleaning compn. comprising 1,2-trans-dichloroethylene (71), Et perfluorobutyl ether (HFE 7200) (28.5), and n-propanol (0.5%) was produced, the compn. forming an **azeotrope** with b.p. of 47.degree. at 1 atm.

IT 100-41-4, **Ethylbenzene**, uses 124-18-5,

**Decane**

(cleaning compns. contg. dichloroethylene and alkoxy substituted perfluoro compds. having six carbon atoms)

RN 100-41-4 HCA  
 CN Benzene, ethyl- (7CI, 8CI, 9CI) (CA INDEX NAME)



RN 124-18-5 HCA  
 CN Decane (8CI, 9CI) (CA INDEX NAME)

Me- (CH<sub>2</sub>)<sub>8</sub>-Me

IC ICM C11D001-00  
 NCL 510410000; 510177000; 510408000; 510415000  
 CC 46-6 (Surface Active Agents and Detergents)  
 IT **Azeotropes**  
 (cleaning compns. contg. dichloroethylene and alkoxy substituted  
 perfluoro compds. having six carbon atoms)  
 IT 57-55-6, Propylene glycol, uses 60-29-7, Diethyl ether, uses  
 64-17-5, Ethanol, uses 67-56-1, Methanol, uses 67-63-0,  
 Isopropanol, uses 67-64-1, Acetone, uses 71-23-8, n-Propanol,  
 uses 71-36-3, Butyl alcohol, uses 71-41-0, 1-Pentanol, uses  
 71-43-2, Benzene, uses 74-84-0, Ethane, uses 74-87-3, Methyl  
 chloride, uses 74-89-5, Methylamine, uses 74-98-6, Propane, uses  
 75-00-3, Ethyl chloride 75-04-7, Ethylamine, uses 75-09-2,  
 Methylene chloride, uses 75-21-8, Ethylene oxide, uses 75-28-5,  
 2-Methylpropane 75-29-6, Isopropyl chloride 75-31-0,  
 Isopropylamine, uses 75-50-3, Trimethylamine, uses 75-56-9,  
 Propylene oxide, uses 75-64-9, tert-Butylamine, uses 75-65-0,  
 tert-Butyl alcohol, uses 75-89-8 76-16-4, Perfluoroethane  
 76-19-7, Perfluoropropane 78-78-4, Isopentane 78-81-9,  
 Isobutylamine 78-86-4, sec-Butyl chloride 78-92-2, 2-Butanol  
 78-93-3, Methyl ethyl ketone, uses 79-20-9, Methyl acetate  
 95-63-6, Pseudocumene 96-22-0, 3-Pentanone 96-41-3,  
 Cyclopentanol 97-99-4, Tetrahydrofurfuryl alcohol 98-00-0,  
 Furfuryl alcohol 98-08-8, Benzotrifluoride 98-82-8, Cumene  
**100-41-4, Ethylbenzene**, uses 100-51-6, Benzyl  
 alcohol, uses 100-66-3, Anisole, uses 102-69-2,  
 Tri-n-propylamine 102-71-6, Triethanolamine, uses 104-51-8,  
 Butylbenzene 104-76-7, 2-Ethylhexanol 105-37-3, Ethyl propionate  
 105-54-4, Ethyl butyrate 105-66-8, Propyl butyrate 106-36-5,  
 Propyl propionate 106-65-0, Dimethyl succinate 106-94-5, Propyl  
 bromide 106-97-8, Butane, uses 107-10-8, n-Propylamine, uses  
 107-18-6, Allyl alcohol, uses 107-21-1, Ethylene glycol, uses  
 107-31-3, Methyl formate 107-46-0, Hexamethyl disiloxane

107-51-7, Octamethyl trisiloxane 107-83-5, Isohexane 107-87-9,  
2-Pentanone 108-10-1, Methyl isobutyl ketone 108-18-9,  
Diisopropylamine 108-20-3, Isopropyl ether 108-59-8, Dimethyl  
malonate 108-67-8, Mesitylene, uses 108-88-3, Toluene, uses  
108-93-0, Cyclohexanol, uses 108-95-2, Phenol, uses 109-21-7,  
Butyl butyrate 109-60-4, Propyl acetate 109-66-0, Pentane, uses  
109-69-3, Butyl chloride 109-73-9, n-Butylamine, uses 109-86-4,  
Ethylene glycol methyl ether 109-87-5, Methylal 109-89-7,  
Diethylamine, uses 109-93-3, Vinyl ether 109-94-4, Ethyl formate  
109-99-9, THF, uses 110-27-0, Isopropyl myristate 110-36-1,  
Butyl myristate 110-54-3, Hexane, uses 110-74-7, Propyl formate  
110-80-5, Ethylene glycol ethyl ether 110-82-7, Cyclohexane, uses  
111-27-3, 1-Hexanol, uses 111-42-2, Diethanolamine, uses  
111-43-3, Propyl ether 111-65-9, Octane, uses 111-76-2, Ethylene  
glycol butyl ether 111-77-3, Diethylene glycol methyl ether  
111-84-2, Nonane 111-87-5, 1-Octanol, uses 111-90-0, Diethylene  
glycol ethyl ether 112-30-1, 1-Decanol 112-34-5, Diethylene  
glycol butyl ether 112-53-8, 1-Dodecanol 115-10-6, Methyl ether  
121-44-8, Triethylamine, uses 123-25-1, Diethyl succinate  
123-86-4, Butyl acetate 123-91-1, 1,4-Dioxane, uses  
**124-18-5, Decane** 124-40-3, Dimethylamine, uses  
124-68-5 138-86-3, Dipentene 141-28-6, Diethyl adipate  
141-43-5, Ethanolamine, uses 141-62-8, Decamethyl tetrasiloxane  
141-78-6, Ethyl acetate, uses 142-68-7, Tetrahydropyran  
142-82-5, Heptane, uses 142-84-7, Di-n-propylamine 142-96-1,  
Butyl ether 287-92-3, Cyclopentane 354-33-6, Pentafluoroethane  
355-25-9, Perfluorobutane 355-42-0, Perfluorohexane 377-36-6,  
1,1,2,2,3,3,4,4-Octafluorobutane 460-35-5, 3-Chloro-1,1,1  
trifluoropropane 462-95-3, Ethylal 507-20-0, tert-Butyl chloride  
513-36-0, Isobutyl chloride 526-73-8, Hemimellitene 540-54-5,  
Propyl chloride 543-59-9, Pentyl chloride 544-01-4, Isoamyl  
oxide 544-10-5, Hexyl chloride 553-90-2, Dimethyl oxalate  
554-12-1, Methyl propionate 557-40-4, Allyl ether 584-02-1,  
3-Pentanol 589-38-8, 3-Hexanone 590-01-2, Butyl propionate  
591-78-6, 2-Hexanone 592-84-7, Butyl formate 616-45-5,  
Pyrrolidone 623-37-0, 3-Hexanol 623-42-7, Methyl butyrate  
626-93-7, 2-Hexanol 627-73-6, Ethyl methyl succinate 627-93-0,  
Dimethyl adipate 637-92-3 646-06-0, 1,3-Dioxolane 678-26-2,  
Perfluoropentane 693-65-2 828-35-3, 1,1,2,2,3,3,4,5-  
Octafluorocyclopentane 872-50-4, N-Methylpyrrolidone, uses  
1119-40-0, Dimethyl glutarate 1300-21-6, Dichloroethane  
1320-67-8, Propylene glycol methyl ether 1320-94-1 1330-16-1,  
Pinene 1330-20-7, Xylene, uses 1634-04-4, Methyl tert-butyl  
ether 1678-91-7, Ethylcyclohexane 2687-91-4, N-Ethylpyrrolidone  
2807-30-9, Ethylene glycol propyl ether 3424-21-3,  
Triisopropylamine 3445-11-2 3470-99-3, N-Propylpyrrolidone  
4838-65-7 5989-27-5, D-Limonene 6032-29-7, 2-Pentanol  
6881-94-3 7803-49-8, Hydroxylamine, uses 8006-39-1, Terpinol

13952-84-6, sec-Butylamine 14303-70-9, Propyl myristate  
 15438-71-8, 1-Hydroxymethyl-2-pyrrolidinone 18891-13-9, Ethyl  
 methyl adipate 19430-93-4 25265-68-3, Methyltetrahydrofuran  
 25265-71-8, Dipropylene glycol 25265-75-2, Butylene glycol  
 26249-20-7, Butylene oxide 26447-60-9, Octafluorobutane  
 26638-19-7 27070-61-7, Hexafluoropropane 27195-67-1,  
 Dimethylcyclohexane 28987-04-4 29387-86-8, Propylene glycol  
 butyl ether 29470-95-9 29759-38-4, Tetrafluoroethane  
 29911-27-1, Dipropylene glycol propyl ether 30136-13-1, Propylene  
 glycol propyl ether 30320-28-6 30423-63-3 30521-24-5  
 33660-75-2, Heptafluoropropane 34077-87-7, Dichlorotrifluoroethane  
 34590-94-8, Dipropylene glycol methyl ether 35884-42-5,  
 Dipropylene glycol butyl ether 37145-47-4, Pentafluoropropane  
 38436-17-8, Nonafluorohexane 38719-68-5, Dimethylbutane  
 43133-95-5, Methylpentane 51000-94-3 51001-25-3,  
 Methyltetrahydropyran 55949-54-7, Nonafluorobutane 61623-04-9  
 72923-37-6 74469-62-8, Hexafluorobutane 76083-84-6 86498-66-0,  
 Dodecafluorohexane 90278-00-5 90278-01-6 102526-10-3,  
 1,1,1,3,3,5,5,5-Octafluoropentane 108662-83-5 116866-99-0,  
 Heptafluorobutane 127564-83-4 127564-91-4 127564-92-5,  
 Dichloropentafluoropropane 133452-70-7, Tridecafluorohexane  
 134190-50-4 134237-36-8 138495-42-8, HFC 43-10MEE 139063-93-7  
 148565-53-1 154275-17-9, Undecafluorohexane 154275-19-1,  
 Octafluorohexane 154275-56-6 155072-58-5, Decafluorohexane  
 163702-07-6, 1,1,1,2,2,3,3,4,4-Nonafluoro-4-methoxybutane  
 186493-81-2 186493-83-4 219484-64-7, HFE 7100 519154-84-8  
 (cleaning compns. contg. dichloroethylene and alkoxy substituted  
 perfluoro compds. having six carbon atoms)

L35 ANSWER 2 OF 20 HCA COPYRIGHT 2005 ACS on STN

62:44073 Original Reference No. 62:7807a-h,7808a-h,7809a-g Terpenoids.  
 LXII. Constitution of agarospirol, a sesquiterpenoid with a new  
 skeleton. Varma, K. R.; Maheshwari, M. L.; Bhattacharyya, S. C.  
 (Nat'l. Chem. Lab., Poona, India). Tetrahedron, 21(1), 115-38  
 (English) 1965. CODEN: TETRAB. ISSN: 0040-4020. OTHER SOURCES:  
 CASREACT 62:44073.

GI For diagram(s), see printed CA Issue.

AB cf. CA 59, 15321f; preceding abstr. Alc. fractions of oil from  
 Aquilaria agallocha chromatographed over 50-fold amts. of Al2O3  
 (grade II), the latter fraction (15 g.) refluxed 6 hrs. at  
 150-60.degree. with 15 g. freshly fused NaOAc and 75 ml. Ac2O, and  
 the crude acetate (17.7 g.) chromatographed over Al2O3 and eluted  
 with 17:3 petr. ether-C6H6 gave 10 g. agarospirol (I) acetate, b0.5  
 130.degree., [ $\alpha$ ]<sub>D</sub> 11.33.degree. (c 9.52), n<sub>D</sub> 1.4892. The  
 acetate (28.82 g.) kept 17 hrs. at 25.degree. in 110 ml. 10% alc.  
 KOH, the mixt. dild. with 600 ml. H2O and extd. 3 times with 150 ml.  
 Et2O, the crude alc. (24.5 g.) chromatographed over 500 g. Al2O3 and  
 eluted with Et2O, and the eluate distd. gave I, b0.1



90-1.degree., [.alpha.]27D -5.7.degree. (c 28.7), n27D 1.5080, d2525 0.9797. I. (1.0 g.) in 10 ml. CHCl3 kept 24 hrs. at 0.degree. with 1.2 moles BzO2H in CHCl3 (0.92N) gave 0.95 g. epoxide, m. 109-10.degree. (petr. ether), [.alpha.]28D 44.78.degree.. I (2.56 g.) in 60 ml. AcOH hydrogenated 5 hrs. at 22.degree. with 150 mg. prereduced PtO2, the filtered soln. extd. with 255 ml. Et2O, and the product (2.57 g.) chromatographed over 40 g. Al2O3 (grade III) and eluted with 200 ml. C6H6 gave 2.49 g. viscous oily dihydroagarospirol (II), b0.4 118.degree., [.alpha.]27D 18.94.degree. (c 12.98), n26D 1.4962; benzoate, viscous oil, b0.2 180.degree., [.alpha.]28D 0.72.degree. (c 5.6), n28D 1.5240. Pyrolysis of the benzoate followed by chromatography over Al2O3 and **distn.** over Na yielded 90% monoene (III), [.alpha.]27D 15.39.degree. (c 10.47), n30D 1.4920. I. (1.6 g.) in 5 ml. C5H5N kept 24 hrs. at 25.degree. with 2 ml. BzCl and heated 20 min. with 30 ml. H2O at 100.degree., the cooled mixt. extd. with 100 ml. Et2O, and the extd. benzoate chromatographed over 50 g. Al2O3 gave I benzoate, b0.2 175.degree., [.alpha.]27D 5.96.degree., n28D 1.5279. The benzoate (1.6 g.) heated 30 min. at 220-30.degree./100 +/- 5 mm., the combined residue and **distillate** chromatographed on 50 g. Al2O3 and eluted with 150 ml. petr. ether, and the product (1.03 g.) **distd.** over Na gave the pure diene (IV), C15H24, b3.0 118.degree., [.alpha.]27D -1.98 (c 14.64), n27D 1.5046, d2525 0.9156. Attempted isomerization with Li-NHCH2CH2NHLi, HClO4-AcOH, BF3.Et2O, or HCO2H gave no appreciable amt. of conjugated product suggesting the presence of an uncommon ring system of the spiro type in I. IV (1.34 g.) in 60 ml. abs. MeOH hydrogenated by stirring with 200 mg. 5% Pd-C with adsorption of 185 ml. H (equiv. to 1.08 double bond) and the filtered soln. evapd. gave a mixt. of IV, monoene (V), and agarospiroane (VI) in the ratio 15:75:10 by gas chromatographic analysis, sepd. by elaborate column chromatography over 1000-fold amts. of Al2O3 (grade I) to give 0.70 g. monoene, **distd.** over Na to yield pure V, C15H26, b3.3 118.degree., [.alpha.]28D 4.8.degree. (c 5.0), n30D 1.4900. IV (500 mg.) in 20 ml. AcOH hydrogenated 4 hrs. with 50 mg. prereduced PtO2, the filtered soln. dild. with 60 ml. H2O and extd. with 50 ml. petr. ether, and the satd. hydrocarbon (480 mg.) kept 24 hrs. at 0.degree. in 5 ml. 0.52N BzO2H-CHCl3, chromatographed on 25 g. Al2O3, and eluted with 50 ml. petr. ether yielded VI, b3.0 112.degree., [.alpha.]30D 19.88.degree. (c 10.5), n31D 1.4772. The monoene III (3.45 g.) in 60 ml. CHCl3 ozonized at 0.degree. 6 hrs., the solvent evapd. in vacuo, the residue heated 3 hrs. in 30 ml. H2O on a steam bath with evolution of 70% HCHO and 15% Me2CO, the nonvolatile portion extd. with Et2O, the oily product (3.0 g.) chromatographed over 150 g. Al2O3 and eluted with 100 ml. to recover 965 mg. III, and the column further eluted with 100 ml. petr. ether to give a mixt. of ketone (VII) and ester (VIII) and eluted with 900 ml. petr. ether gave 815 mg. XII, further purified by rechromatography to give

pure material, b3.5 140.degree.,  $[\alpha]_D^{27} -0.35$ .degree. (c 6.0); epimeric 2,4-dinitrophenylhydrazones m. 147-9.degree., 118-23.degree. (more sol. in EtOH); epimeric semicarbazone mixt. m. 193-5.degree. (alc.). Further elution with 9:1 petr. ether C6H6 and rechromatography of the product (513 mg.) gave the ketone (IX), b3.5 130.degree.; epimeric 2,4-dinitrophenylhydrazones m. 194-6.degree. and 201-3.degree.. VII (450 mg.) in 5 ml. CHCl3 contg. a catalytic amt. of p-MeC6H4SO3H kept 48 hrs. at 0.degree. with 6 ml. 0.9N BzO2H-CHCl3 and the ester, refluxed 1 hr. in 10 ml. 5% alc. KOH, followed by chromatography over 7 g. Al2O3 gave the pure alc. (212 mg.) free from VII. The alc. in 3 ml. AcOH kept 3 hrs. at 25.degree. with 150 mg. CrO3 in 6 ml. 1:1 H2O-AcOH, excess CrO3 decompd. with MeOH, dild. with 30 ml. H2O, and extd. 3 times with 20 ml. Et2O, and the crude ketonic product chromatographed over 3 g. Al2O3 and eluted with 30 ml. 4:1 petr. ether-C6H6 gave IX. IX (30 mg.) in 2 ml. CHCl3 contg. p-MeC6H4-SO3H oxidized 48 hrs. at 0.degree. with 3 ml. 0.9N BzO2H-CHCl3, the product refluxed 2 hrs. in 5 ml. 5% alc. KOH, dild. with H2O, and extd. with 30 ml. Et2O, the aq. layer acidified with dil. HCl and extd. with 30 ml. Et2O, and the crude **lactone** chromatographed over 500 mg. Al2O3 and eluted with C6H6 gave 15 mg. pure **lactone** (X), C12H20O2. The mixt. of VII and VIII sapond. and chromatographed gave VII and an alc. portion, oxidized to yield IX. V (3.25 g.) in 10 ml. dry CHCl3 kept 24 hrs. at 0.degree. in 42 ml. 1.0N BzO2H-CHCl3 and the product (3.23 g.) chromatographed over 130 g. Al2O3 (grade II) and eluted with petr. ether gave a middle fraction contg. 2.2 g. 98% pure epoxide (XI), b1.0 120.degree.,  $[\alpha]_D^{27} 11.32$ .degree. (c 6.185), n28D 1.4845, purified by chromatography and pyrolyzed as the benzoate to furnish a hydrocarbon mixt. XI (730 mg.) in 10 ml. C6H6 kept 1 hr. at 25.degree. with 0.3 ml. BF3.Et2O and the product chromatographed on 40 g. Al2O3 (grade II) and eluted with petr. ether and 4:1 petr. ether-C6H6 gave 90 mg. XI and 300 mg. ketone (XII),  $[\alpha]_D^{27} 15.70$ .degree. (c 9.175), n29D 1.4860. Further elution with 3:2 petr. ether-C6H6 furnished 225 mg. viscous oily enolic  $\alpha$ -ketol, b0.2 160.degree.  $[\alpha]_D^{30} 2.43$ .degree. (c 8.62). V (620 mg.) in 20 ml. purified tetrahydrofuran contg. a trace of ZnCl2 treated at 0.degree. with B2H6 1.5 hrs., the mixt. kept 1.0 hr. at 25.degree., treated at 0.degree. with 10 ml. 12% aq. NaOH and 10 ml. 30% H2O2 in 1 hr., and kept 2 hrs. at 0.degree. the org. layer and Et2O washings evapd., and the residue (580 mg.) chromatographed over 10 g. Al2O3, washed with 50 ml. Et2O to remove 100 mg. V, and eluted with C6H6 gave an epimeric mixt. (30:7) of the monol (XIII), b0.8 140.degree.,  $[\alpha]_D^{27} 12.23$ .degree. (c 3.93), n27.5D 1.4913. XIII (170 mg.) in 3 ml. AcOH kept 1 hr. at 25.degree. with 120 mg. CrO3 in 4 ml. AcOH contg. 4 drops of H2O, dild. with H2O, and extd. with Et2O, the product chromatographed over 10 g. Al2O3 and eluted with 50 ml. 4:1 petr. ether-C6H6, and the eluate **distd.** yielded 130 mg.

epimeric mixt. (31:69) of the ketone XII, b0.35 118.degree., [.alpha.]<sub>D</sub><sup>27</sup> 16.92.degree. (c 2.24), n<sub>D</sub><sup>27</sup> 1.4833. The mixt. (60 g.) heated 6 hrs. on a steam bath with 100 mg. K in 10 ml. Me<sub>3</sub>COH, dild. with H<sub>2</sub>O, and extd. with Et<sub>2</sub>O and the solvent evapd. gave 48 mg. ketone (epimeric mixt. 13:87), converted to a liquid 2,4-dinitrophenylhydrazone, purified by chromatography over 10 g. Al<sub>2</sub>O<sub>3</sub>, and eluted with 30 ml. 9:1 petr. ether-C<sub>6</sub>H<sub>6</sub> to give 10 mg. material and with 20 ml. 1:1 petr. ether-C<sub>6</sub>H<sub>6</sub> yielded 26 mg. orange needles, m. 179-80.degree. (alc.). XI (1.0 g.) heated 2 hrs. on a water bath with 10 ml. AcOH, the residue on evapn. chromatographed on 30 g. Al<sub>2</sub>O<sub>3</sub> and eluted with 100 ml. 4:1 petr. ether-C<sub>6</sub>H<sub>6</sub>, and the impure enol acetate (220 mg.) sapond. gave XII, identified as the 2,4-dinitrophenylhydrazone. Further elution with 100 ml. Et<sub>2</sub>O and sapon. of the product (620 mg.) gave the trans-diol (XIV), b0.13 133.degree., [.alpha.]<sub>D</sub><sup>28</sup> 9.8.degree. (c 6.5), n<sub>D</sub><sup>29</sup> 1.5028. V (800 mg.) kept 6 days with 1.0 g. OsO<sub>4</sub> in 25 ml. Et<sub>2</sub>O and 4 ml. C<sub>5</sub>H<sub>5</sub>N, the ppt. refluxed 4 hrs. with 5.0 g. KOH and 5.0 g. mannitol in 150 ml. 1:1:1 C<sub>6</sub>H<sub>6</sub>-MeOH-H<sub>2</sub>O and dild. with 100 ml. H<sub>2</sub>O, the org. layer and 150 ml. C<sub>6</sub>H<sub>6</sub> washings evapd., the residue (690 mg.) chromatographed, the column washed with 70 ml. petr. ether to remove 280 mg. V and eluted with 50 ml. 9:1 C<sub>6</sub>H<sub>6</sub>-Et<sub>2</sub>O, and the eluate **distd.** yielded 380 mg. cis-diol (XIVa), b15 140.degree., n<sub>D</sub><sup>28</sup>. XIVa (150 mg.) in 6 ml. dioxane stirred 3 hrs. with 150 mg. NaIO<sub>4</sub> in 13 ml. H<sub>2</sub>O and the dild. soln. extd. with Et<sub>2</sub>O gave 135 mg. hydroxyaldehyde (XV). V (750 mg.) in 25 ml. EtOAc at -20.degree. ozonized 3 hrs., the product hydrogenated with 150 mg. 10% Pd-C 2 hrs., the soln. filtered, and the solvent removed in vacuo yielded 700 mg. viscous oil, also obtained by NaIO<sub>4</sub> oxidn. of XIVa. The oil (600 mg.) in 20 ml. MeOH stirred 24 hrs. in the dark with 1.0 g. Ag<sub>2</sub>O the mixt. stirred 24 hrs. with 300 mg. KOH in 5 ml. MeOH and 3 ml. H<sub>2</sub>O, dild. with H<sub>2</sub>O, and extd. with Et<sub>2</sub>O, the aq. layer acidified with cold dil. HCl and after satn. with NH<sub>4</sub>Cl extd. with Et<sub>2</sub>O, the Et<sub>2</sub>O exts. evapd., the product (300 mg.) in 20 ml. Et<sub>2</sub>O treated with a calcd. amt. of ethereal CH<sub>2</sub>N<sub>2</sub> at 0.degree., excess CH<sub>2</sub>N<sub>2</sub> decompd. with AcOH, and the solvent removed gave 105 mg. ester (XVI), b0.2 127.degree., n<sub>D</sub><sup>28</sup> 1.4720. The uv spectrum was strikingly similar to those of 1-carbomethoxy-2-methylcyclopent-1(2)-ene and Me isolauranolate but different from that of 1-carbomethoxycyclopent-1(2)-ene, thus suggesting the assigned structure for XV. The relative disposition of the alkyl substituents in I was established by dehydrogenation. I. (1.63 g.) heated with 1.6 g. Se (N atm.) 18 hrs. at 285-90.degree. and the product chromatographed on 50 g. Al<sub>2</sub>O<sub>3</sub> and eluted with 300 ml. petr. ether, the eluate washed with H<sub>3</sub>PO<sub>3</sub> to remove 20 mg. azulenes, the residue (1.43 g.) treated with picric acid, and the eudalene picrate, m. 93.0-4.5.degree. decompd. over Al<sub>2</sub>O<sub>3</sub> gave eudalene, identified as the trinitrobenzene adduct, m. 110-11.degree. (alc.). II, III, IV, and V under similar conditions yielded 6.5-7.8, 7-10,

32-4, and 24-28% eudalene, resp. Accordingly, only 2 structures (I and XVII) were possible for agarospirol and differentiation was obtained by labeling followed by dehydrogenation and also by an unambiguous synthesis of IX starting from 2,6-dimethylcyclohexanone. MeI (4.7 ml.) refluxed 4 hrs. with 1.4 g. Li in 40 ml. Et<sub>2</sub>O with stirring, the clear soln. refluxed 48 hrs. with 350 mg. ketone XII in 10 ml. Et<sub>2</sub>O, excess reagent decompd. with aq. Na<sub>2</sub>SO<sub>4</sub> contg. some Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, the washed and dried Et<sub>2</sub>O layer evapd., the residue chromatographed over 10 g. Al<sub>2</sub>O<sub>3</sub>, and the eluate evapd. gave 240 mg. carbinol (XVIII). Dehydrogenation of XVIII with Se gave 1,4-dimethyl-6-isopropyl-naphthalene, identified as the picrate, m. 101-2.degree., and sym. trinitrobenzene adduct, m. 135-6.degree. (alc.). These observations supported I as the only possible structure for agarospirol and were confirmed by an unambiguous synthesis of the derived ketone X. Prepn. from .omicron.-methylcyclohexanone by the method of Johnson and Posvic (CA 41, 6537c) gave 80% 6-hydroxymethylene-2-methylcyclohexanone, methylated and the mixt. hydroxymethylated yielded 62% 2,6-dimethylcyclohexanone, b<sub>718</sub> 173-4.degree.. Conversion according to Cope and Hancock [Org. Syntheses Collective Vol. III, 398-401(1955)] using a larger amt. of NH<sub>4</sub>OAc-HOAc and 6 hrs. reaction time yielded 40% alkylidene ester (XIX), b<sub>0.5</sub> 126-8.degree., n<sub>28D</sub> 1.4855. MeOH (75 ml.) contg. 2.08 g. Na stirred at 0.degree. with 7.602 g. NCCH<sub>2</sub>CONH<sub>2</sub> and the clear soln. treated in 3 installments with 10 g. XIX in 25 ml. MeOH, kept 24 hrs. at 25.degree., dild. with 200 ml. H<sub>2</sub>O, and washed twice with 50 ml. H<sub>2</sub>O and the aq. layer acidified with cold dil. HCl yielded 38.3% .beta.-2,6-dimethylcyclohexylidene-.alpha.,.alpha.'-dicyanoglutarimide (XX), m. 254-5.degree. (decompn.). XX (2.4 g.) heated 1 hr. at 170.degree. in 6 ml. concd. H<sub>2</sub>SO<sub>4</sub> and 1.6 ml. H<sub>2</sub>O, the mixt. refluxed 1 hr. in 10 ml. H<sub>2</sub>O, the black ppt. taken up in alc. (C), the decolorized soln. concd. and dild. with C<sub>6</sub>H<sub>6</sub>, and the ppt. recovered from alc. with C<sub>6</sub>H<sub>6</sub> gave the diacid (XXI, R = H), m. 189.degree. (decompn.). The acid (6.0 g.) in 20 ml. abs. alc. and 40 ml. C<sub>6</sub>H<sub>6</sub> contg. 0.2 ml. concd. H<sub>2</sub>SO<sub>4</sub> **azeotropically** refluxed 24 hrs. under a Dean-Stark head yielded 83% XXI (R = Et) (XXII), b<sub>0.35</sub> 110.degree.. Xylene (400 ml.) vigorously stirred under reflux (N atm.) 30 min. with 2.0 g. Na and 2.0 g. K with passage of 50 ml. solvent, 4.5 g. XXII in 50 ml. xylene added in 1 hr., the mixt. refluxed 1.5 hrs., excess alloy decompd. at 0.degree. with alc. and stirring with 50 ml. 18% HCl, the H<sub>2</sub>O-washed xylene layer evapd. (N atm.) in vacuo, the residue (2.54 g.) chromatographed over 40 g. AcOH-deactivated Al<sub>2</sub>O<sub>3</sub> and eluted with 100 ml. 17:3 petr. ether-C<sub>6</sub>H<sub>6</sub>, and the mixt. (1.2 g.) of satd. hydrocarbon, b<sub>1.0</sub> 183.degree., n<sub>28.5D</sub> 1.4688, oxo ester (XXIII), and ketone (XXIV), sepd. by chromatography to give 210 mg. pure XXIII, and 620 mg. pure XXIV, b<sub>4.0</sub> 135.degree.; 2,4-dinitrophenylhydrazone m. 212-13.degree. (alc.). Further elution with 150 ml. Et<sub>2</sub>O gave 810 mg. acyloin (XXV), b<sub>0.1</sub>

128.degree.. XXV (800 mg.) converted to the p-tolylsulfonate and added (1.32 g.) in 20 ml. anhyd. Et2O to 700 mg. LiAlH4 in 30 ml. Et2O, the mixt. refluxed 10 hrs., excess reagent decompd. with dil. alc. and dil. HCl, the org. layer and Et2O washings evapd., the monol (513 mg.) oxidized in 15 ml. AcOH contg. 500 mg. CrO3 1 hr., the oxidn. product chromatographed over 20 g. neutral Al2O3, eluted with 70 ml. petr. ether to remove 140 mg. hydrocarbon (XXVI), and eluted with 50 ml. petr. ether-C6H6 and the eluate **distd.** gave 200 mg. IX, bl.5 117.degree., contg. 2 epimers in 55:45 ratio; 2,4-dinitrophenylhydrazone m. 179-82.degree..

CC 40 (Terpenes)

IT Agarospirol, dihydro-, benzoate

Agarospirol, epoxydihydro-

Ketone, 6,10-dimethylspiro[4.5]dec-2-yl methyl, (2,4-dinitrophenyl)hydrazone, epimers

Ketone, 6,10-dimethylspiro[4.5]dec-2-yl methyl, epimers

Ketone, 6,10-dimethylspiro[4.5]dec-2-yl methyl, semicarbazone, epimers

Naphthalene, octahydro-7-isopropenyl-1.beta.,4a.beta.-dimethyl-

Spiro[4.5]dec-6-ene, 2-isopropenyl-6,10-dimethyl-

Spiro[4.5]decan-2-one, 6,10-dimethyl-, (2,4-dinitrophenyl)hydrazone, epimers

Spiro[4.5]decan-2-one, 6,10-dimethyl-, epimers

Spiro[4.5]decan-7-one, 2-isopropyl-6,10-dimethyl-, epimers

Spiro[4.5]**decane**-6,7-diol, 2-isopropyl-6,10-dimethyl-,  
cis-

Spiro[4.5]**decane**-6,7-diol, 2-isopropyl-6,10-dimethyl-,  
trans-

IT 1460-75-9, Agarospirol, dihydro- 1460-77-1, Agarospirol, benzoate  
1460-81-7, Cyclohexaneacetic acid, 1-(2-hydroxyethyl)-2,6-dimethyl-,  
.delta.-**lactone** 1460-82-8, Spiro[cyclopentane-1,2'-  
[7]oxabicyclo[4.1.0]-heptane], 3-isopropyl-1',3'-dimethyl-  
1460-84-0, Spiro[4.5]decan-7-ol, 2-isopropyl-6,10-dimethyl-  
1460-85-1, Spiro[4.5]decan-7-one, 2-isopropyl-6,10-dimethyl-,  
(2,4-dinitrophenyl)hydrazone 1460-86-2, Spiro[4.4]nonane-2-  
carboxaldehyde, 1-hydroxy-7-isopropyl-1,4-dimethyl- 1460-87-3,  
Spiro[4.4]non-1-ene-2-carboxylic acid, 7-isopropyl-1,4-dimethyl-,  
methyl ester 1460-89-5, Spiro[4.5]decan-7-ol, 2-isopropyl-6,7,10-  
trimethyl- 1460-90-8, .DELTA.1,.alpha.-Cyclohexaneacetic acid,  
.alpha.-cyano-2,6-dimethyl-, ethyl ester 1856-35-5,  
1,1-Cyclohexanediacyetic acid, 2,6-dimethyl- 1856-36-6,  
Spiro[3.5]nonane-1-carboxylic acid, 5,9-dimethyl-2-oxo-, ethyl ester  
1856-37-7, Spiro[3.5]nonan-2-one, 5,9-dimethyl- 1856-38-8,  
Spiro[3.5]nonan-2-one, 5,9-dimethyl-, (2,4-dinitrophenyl)hydrazone  
1856-39-9, Spiro[4.5]decan-2-one, 3-hydroxy-6,10-dimethyl-  
1905-59-5, Naphthalene, 6-isopropyl-1,4-dimethyl-, compd. with  
1,3,5-trinitrobenzene (1:1) 2068-50-0, Spiro[4.5]**decane**,  
2-isopropenyl-6,10-dimethyl- 2068-52-2, Spiro[4.5]dec-6-ene,

2-isopropyl-6,10-dimethyl- 3751-08-4, 1,1-Cyclohexanediacetic acid, 2,6-dimethyl-, diethyl ester 3955-55-3, 1,1-Cyclohexanediacetimide, .alpha.,.alpha.'-dicyano-2,6-dimethyl-20479-41-8, Agarospirane 57794-68-0, Agarospirol, acetate (prepn. of)

L35 ANSWER 3 OF 20 HCA COPYRIGHT 2005 ACS on STN

58:81091 Original Reference No. 58:13799c-f Separation of ethylene carbonate from ethylene glycol. Anderson, John R. (Union Carbide Corp.). US 3074962 19630122, 5 pp. (Unavailable). APPLICATION: US 19580422.

AB Mixts. of the title compds. are sepd. by 2 methods. In one method an aromatic hydrocarbon solvent is added to the mixt., and the resultant mixt. is **distd.** at reduced pressure. This removes the glycol and solvent as an **azeotrope**, and the carbonate is left as the residue. In the other method, used for larger amts. of glycol in the mixt., the solvent is added in an extn. column to remove the carbonate and leave the glycol behind. The ext. is then **distd.**, to give the solvent-glycol **azeotrope** and the carbonate residue. On condensing the **azeotrope** separates into layers, and the components are removed by decanting. Suitable solvents are the alkylbenzenes, toluene, **ethylbenzene**, xylenes, etc., and mixts. thereof. Using the first method, a mixt. of 90 parts ethylene carbonate and 10 parts ethylene glycol was fed to a still with 200 parts of com. xylene. The still, having 15 theoretical plates, was operated at 40 mm. and 50.degree.. Removal of the **azeotrope** left 98% pure carbonate. An example of the 2nd method used a 500 parts each mixt. of glycol and carbonate fed with 2009 parts toluene to a York-Scheibel column 2'' inner diam. X 72'' long. Effluents from the column were 2398 parts solvent and carbonate, with some glycol, and 611 parts sepd. glycol. The ext. was fed to a batch stripping still operated with reflux ratio 1:1 at 60 mm. and 40.degree. at the head. The pressure was later reduced to 6 mm., and the head temp. was raised to 80.degree., with kettle temp. up to 125.degree.. The residue was 380 parts ethylene carbonate of 98% purity. Three-component soly. curves are included for glycol-carbonate-toluene and glycolcarbonate-**ethylbenzene** mixts.

NCL 260340200

CC 33 (Aliphatic Compounds)

IT 96-49-1, Carbonic acid, **cyclic ethylene ester**  
(recovery from mixt. with ethylene glycol)

L35 ANSWER 4 OF 20 HCA COPYRIGHT 2005 ACS on STN

58:53204 Original Reference No. 58:9042d-h,9043a-b The action of a-mercaptocarboxylic acid on unsaturated .beta.-aminocarboxylic acid esters. Asinger, Friedrich; Fabian, Juergen (Tech. Hochschule, Dresden, Germany). Monatshefte fuer Chemie, 93, 282-91

(Unavailable) 1962. CODEN: MOCMB7. ISSN: 0026-9247. OTHER SOURCES: CASREACT 58:53204.

AB .alpha.-Mercaptocarboxylic acids and their esters refluxed in tech. CHCl<sub>3</sub> with .beta.-aminocrotonic ester analogs with tile **azeotropic** removal of H<sub>2</sub>O yield 2-carbalkoxymethyl-1,3-thiazolid-4-ones, but Et g-cyclohexylaminocrotonate (I) and iso-PrNHC-Me:CHCO<sub>2</sub>Et (II) with HSCH<sub>2</sub>CO<sub>2</sub>H (III) give the corresponding .beta.-acetylthiotetronic acid amides. AcCH<sub>2</sub>CO<sub>2</sub>Et (59 g.), 32 g. HSCH<sub>2</sub>CO<sub>2</sub>Me, 150 cc. abs. EtOH, and 7.5 cc. abs. alc. HCl kept 3 days at room temp. and fractionated, the resulting MeO<sub>2</sub>CCH<sub>2</sub>SCMe. CHCO<sub>2</sub>Et (20 g.), b<sub>0.4</sub> 122-8.degree., treated immediately with 10 cc. concd. NH<sub>4</sub>OH, dild. with MeOH to soln., kept 2 days at room temp., and filtered yielded 4.1 g. H<sub>2</sub>ONO-CCH<sub>2</sub>SCMe: CHCO<sub>2</sub>Et (IV), m. 108.degree. (aq. MeOH). III (0.4 mole) and 0.25 mole appropriate enamine in 250 cc. tech. CHCl<sub>3</sub> refluxed 30-40 hrs. with the **azeotropic** removal of the H<sub>2</sub>O, cooled, washed with 5% NH<sub>4</sub>OH, dried, and evapd. gave 66% 2-methyl-2-carbethoxymethyl-4-thiazolidone (V), b<sub>0.06</sub> 132.degree., in. 55-6.degree.. A series of similar runs with 0.5 mole III, 0.25 mole .beta.-aminocrotonic acid Et ester and 250 cc. of various solvents was performed (solvent used, reaction time in hrs., and % yield of V given): iso-Pr<sub>2</sub>O + 1 cc. HCO<sub>2</sub>H, 24, 23; pure CHCl<sub>3</sub>, 24, 37; CCl<sub>4</sub>, 24, 10; C<sub>6</sub>H<sub>6</sub>, 24, 34; C<sub>6</sub>H<sub>6</sub> + 1 g. p-MeC<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>H, 31, 43; C<sub>6</sub>H<sub>6</sub> + 1 cc. C<sub>5</sub>H<sub>5</sub>N, 31, 38; xylene, 24, 10. By the same method as V were prepd. the following compds. (% yield, b.p./mm., m.p., and n<sub>D</sub><sup>20</sup> given): 2-methyl-2-carbomethoxymethyl-4-thiazolidone, 30, 134.degree./0.1, --, 1.5207; 3-Me deriv. of V, 70, 121.degree./0.15, --, 1.5057; 3-PhCH<sub>2</sub> deriv. of V, 57, 180.degree./0.2, --, 1.5538; 5-Me deriv. of V, 62, --, 63-4.degree., --; 2-methyl-2-(1'-methyl-1'-carbethoxymethyl)-4-thiazolidone (VI), 41, 151.degree./0.5, 65-6.degree., --; 1'-Pr analog of VI, 47, --, 77-9% --; 1'-PhCH<sub>2</sub> analog of VI, 52, 190-2.degree./0-4, --, --; 2,2-dicarbethoxymethyl-4-thiazolidone, 33, 174-5.degree./0.3, 50-1.5.degree., --; 2,2-(1'-carbethoxypentamethylene)-4-thiazolidone, 61, --, 89-90.degree., --. The appropriate .alpha.-mercaptocarboxylic acid (0.4 mole), 0.25 mole suitable .beta.-oxocarboxylic acid esters, 31 g. NH<sub>4</sub>OAc, and 250 cc. C<sub>6</sub>H<sub>6</sub> refluxed 24 hrs. with the **azeotropic** removal of H<sub>2</sub>O gave 30% 2-methyl-2-(1',1'-diethyl-1'-carbethoxymethyl)-4-thiazolidone, m. 93.5, 94.degree., and 48% 2-propyl-2-(1'-ethyl-1'-carbethoxynlethyl)-4-thiazolidone, b<sub>0.1</sub> 147-8.degree., n<sub>D</sub><sup>20</sup> 1.4991. V (10 g.) and 10 cc. 30% aq. NaOH warmed with shaking to 30.degree., cooled immediately, washed with 10 cc. EtOAc, acidified with cooling with 20% H<sub>2</sub>SO<sub>4</sub>, and extd. with EtOAc yielded 6.8 g. 2-methyl-2-carboxymethyl-4-thiazolidone, powder, m. 135.6.degree.. V (20 g.), 150 cc. concd. NH<sub>4</sub>O H, and 250 cc. MeOH (satd. with NH<sub>3</sub>) kept 24 hrs. at room temp. and concd. gave 2.4 g. 2-methyl-2-carbamoylmethyl-4-thiazolidone. V (7.1 g.) in AcOH treated with 100 cc. 8% KMnO<sub>4</sub> in portions, kept 2 hrs.,

decolorized with SO<sub>2</sub>, and refrigerated overnight yielded 6.1 g. 1,1-dioxide of V, m. 138-9.degree. (EtOH and C<sub>6</sub>H<sub>6</sub>). I. (53 g.) and 37 g. III in 250 cc. C<sub>6</sub>H<sub>6</sub> refluxed 36 hrs. with 1 g. p-MeC<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>H with the removal of 4 cc. H<sub>2</sub>O, washed with 5% NH<sub>4</sub>OH, and evap., gave 21 g. .alpha.-acetylthiotetronic acid cyclohexyl-amide (VII), m. 127.degree. (EtOH). VII and N NaOH heated 1 hr. on the water base, and the liberated base treated with PhNCS gave N-phenyl-N'-cyclohexylurea; the aq. alk. phase acidified gave .alpha.-acetylthiotetronic acid, m. 89.degree. (EtOH). II (43 g.) and 37 g. III gave in the usual manner 12 g. .alpha.-acetylthiotetronic acid iso-propylamide (VIII), needles, m. 125-6.degree. (EtOH and dioxane). AcCH<sub>2</sub>CO<sub>2</sub>Et (32 g.), 11 g. HCONH<sub>2</sub>, and 37 g. III in 250 cc. CHCl<sub>3</sub> refluxed 48 hrs. with the **azeotropic** removal of 6.5 cc. H<sub>2</sub>O gave 15 g.

2,6-dimethyl-3,5-dicarbethoxypyridine, m. 70-1.degree. (aq. EtOH). The infrared absorption spectra of IV, V, and VIII are recorded.

CC 38 (Heterocyclic Compounds (More Than One Hetero Atom))

IT 120-75-2, Benzothiazole, 2-methyl- 886-59-9, Urea, 1-cyclohexyl-3-phenyl- 1149-24-2, 3,5-Pyridinedicarboxylic acid, 2,6-dimethyl-, diethyl ester 2049-07-2, 2-Thiazolidineacetic acid, 3-benzyl-2-methyl-4-oxo-, ethyl ester 29942-24-3, 2-Thiazolidineacetic acid, 2-methyl-4-oxo-, ethyl ester 29942-25-4, 2-Thiazolidineacetic acid, 2,5-dimethyl-4-oxo-, ethyl ester 29942-26-5, 2-Thiazolidineacetic acid, 2,3-dimethyl-4-oxo-, ethyl ester 60700-15-4, Acetoacetic acid, 2-acetyl-4-mercapto-, .gamma.-(thio **lactone**) 73964-73-5, Acetoacetic acid, 2-[1-(cyclohexylamino)ethylidene]-4-mercapto-, .gamma.-(thio **lactone**) 89464-53-9, 2-Thiazolidineacetic acid, 2-methyl-4-oxo- 89600-94-2, 2-Thiazolidineacetamide, 2-methyl-4-oxo- 89910-37-2, 2-Thiazolidineacetic acid, 2-methyl-4-oxo-, methyl ester 90088-31-6, Crotonic acid, 3-[(carbamoylmethyl)thio]-, ethyl ester 90088-63-4, 2-Thiazolidineacetic acid, 2-methyl-4-oxo-, ethyl ester, 1,1-dioxide 90609-16-8, 2-Thiazolidineacetic acid, .alpha.,2-dimethyl-4-oxo-, ethyl ester 91005-49-1, Crotonic acid, 3-[(carboxymethyl)thio]-, 1-ethyl methyl ester 91333-86-7, 2-Thiazolidineacetic acid, 2-methyl-4-oxo-.alpha.-propyl-, ethyl ester 91341-25-2, 2,2-Thiazolidinediacetic acid, 4-oxo-, diethyl ester 91691-13-3, 2-Thiazolidineacetic acid, .alpha.,.alpha.-diethyl-2-methyl-4-oxo-, ethyl ester 92100-04-4, 1-Thia-4-azaspiro[4.5]**decane** -8-carboxylic acid, 3-oxo-, ethyl ester 93224-92-1, Acetoacetic acid, 2-[1-(isopropylamino)ethylidene]-4-mercapto-, .gamma.-(thio **lactone**) 94091-97-1, 2-Thiazolidineacetic acid, .alpha.-benzyl-2-methyl-4-oxo-, ethyl ester 96396-24-6, 2-Thiazolidineacetic acid, .alpha.-ethyl-4-oxo-2-propyl-, ethyl ester

(prepn. of)



L35 ANSWER 5 OF 20 HCA COPYRIGHT 2005 ACS on STN

55:137127 Original Reference No. 55:25793b-i,25794a-e Synthesis of 4-carbethoxy-substituted cyclohexenones. Plieninger, Hans; Ege, Gunter; Fischer, Rolf; Hoffmann, Werner (Univ. Heidelberg, Germany). Chemische Berichte, 94, 2106-14 (Unavailable) 1961. CODEN: CHBEAM. ISSN: 0009-2940. OTHER SOURCES: CASREACT 55:137127.

GI For diagram(s), see printed CA Issue.

AB EtO<sub>2</sub>CCH(CHO)CH<sub>2</sub>CO<sub>2</sub>Et (I), CH<sub>2</sub>.CH(CO<sub>2</sub>Et).O.CO.CHCHO (II), and EtO<sub>2</sub>CC(OEt)2CH<sub>2</sub>CH(CHO)CO<sub>2</sub>Et (III) underwent with CH<sub>2</sub>:CHAc (IV) a Michael-type addn.; the products were cyclized by piperidine acetate to the corresponding cyclohexenone derivs. I (120 g.) treated at 0.degree. with stirring with Me<sub>3</sub>COK from 2 g. K and 35 cc. Me<sub>3</sub>COH in 30 cc. C<sub>6</sub>H<sub>6</sub> then dropwise with 42 g. IV below 10.degree., the mixt. kept 20 hrs., dild. with 100 cc. Et<sub>2</sub>O, cooled to -10.degree., washed with N NaOH, and worked up yielded 120 g. AcCH<sub>2</sub>CH<sub>2</sub>C(CO<sub>2</sub>Et)(CHO)CH<sub>2</sub>CO<sub>2</sub>Et (V), b<sub>0.01</sub> 129-33.degree., n<sub>20D</sub> 1.4517; disemicarbazone m. 198.degree. (aq. EtOH). V (68.5 g.), 100 cc. C<sub>6</sub>H<sub>6</sub>, and 4 cc. AcOH refluxed 4.5 hrs. with the **azeotropic** removal of 3.9 cc. H<sub>2</sub>O, cooled, dild. with 100 cc. Et<sub>2</sub>O, and worked up yielded 42 g. 2-cyclohexen-4-one-1-carboxy-1-acetic acid di-Et ester (VI), pale yellow oil. VI (42 g.) in 60 cc. EtOH heated 10 min. on the water bath with 25 g. H<sub>2</sub>NCONHNH<sub>2</sub>.HCl and 25 g. NaOAc in 120 cc. H<sub>2</sub>O yielded 40 g. semicarbazone (VII) of VI, m. 169-70.degree. (aq. EtOH). VII (35 g.), 60 g. AcCO<sub>2</sub>H, 6 cc. AcOH, and 300 cc. H<sub>2</sub>O heated 10 min. to 100.degree., poured onto ice, and extd. with Et<sub>2</sub>O yielded 23 g. VI, b<sub>0.01</sub> 126-30.degree., n<sub>20D</sub> 1.4805; 1,4-dinitrophenylhydrazone m. 130-1.degree.. VI (25.6 g.) in 200 cc. EtOH hydrogenated over Pd-C yielded 23.5 g. cyclohexanone analog (VIII) of VI, b<sub>0.01</sub> 123-5.degree., n<sub>20D</sub> 1.4630; 2,4-dinitrophenylhydrazone, orange, m. 79-80.degree. (aq. EtOH). VIII (1.25 g.) in 5 cc. EtOH refluxed 15 hrs. with 600 mg. KOH and 10 cc. H<sub>2</sub>O, cooled with ice, acidified with 15% HCl, and treated with excess satd. 2,4-(O<sub>2</sub>N)2C<sub>6</sub>H<sub>3</sub>NHNH<sub>2</sub> in 2N HCl gave 1.05 g. cyclohexan-4-one-1-carboxy-1-acetic acid 2,4-dinitrophenylhydrazone, yellow, m. 177-8.degree.. DL-Glutamic acid (300 g.) in 800 cc. H<sub>2</sub>O and 420 cc. concd. HCl treated dropwise at 5.degree. with 140 g. NaNO<sub>2</sub> in 300 cc. H<sub>2</sub>O and then with 70 g. NaNO<sub>2</sub> in 150 cc. H<sub>2</sub>O, the mixt. evapd. after 5 hrs. in vacuo, and extd. with EtOAc gave 239 g. butyrolactone-4-carboxylic acid (IX), b<sub>0.1</sub> 151-6.degree., m. 50-1.degree.. IX (239 g.), 360 cc. EtOH, 900 cc. C<sub>6</sub>H<sub>6</sub>, and 200 mg. p-MeC<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>H refluxed 1 hr. yielded 275 g. Et ester (X) of IX, b<sub>12</sub> 151-5.degree., n<sub>22D</sub> 1.4485. X (10 g.) and 11 cc. SOCl<sub>2</sub> heated 3 hrs. at 80-90.degree. gave the 4-COCl analog of IX, b<sub>12</sub> 136-7.degree., n<sub>20D</sub> 1.4812. X (50 g.), 7 g. Na, and 200 cc. abs. EtOH refluxed 5 hrs., concd., dild. with Et<sub>2</sub>O, neutralized with AcOH, and worked up gave 26 g. EtO<sub>2</sub>CCH(OH)CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>Et (XI), b<sub>12</sub> 135-41.degree., n<sub>20D</sub> 1.4354, and 14 g. less pure XI, b<sub>12</sub> 141-56.degree., n<sub>20D</sub> 1.4479. Abs. EtOH (1 cc.) added to 40 g. powd.

Na in about 1 l. Et<sub>2</sub>O, the mixt. stirred 0.5 hr., treated dropwise with 275 g. X and 258 g. HCO<sub>2</sub>Et, stirred 3 hrs., kept overnight, treated with stirring and cooling with 578 g. 31% H<sub>2</sub>SO<sub>4</sub>, and worked up yielded 145 g. XI, b<sub>0.1</sub> 110-25.degree., and 54 g. II, b<sub>0.1</sub> 120-5.degree., n<sub>22D</sub> 1.4855. A few drops of II in a little 30% HClO<sub>4</sub> treated with 2,4-(O<sub>2</sub>N)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NHNH<sub>2</sub> in 2N HCl gave the 2,4-dinitrophenylhydrazone of II, m. 57-60.degree.. II (0.235 mg.) in MeOH at -10.degree. treated with 30 cc. 3% Br-MeOH, the mixt. decolorized with alc. 2-ClOH<sub>7</sub>OH, treated with 12 cc. about 20% aq. NaI, heated 10 min. at 35-40.degree., cooled to 20.degree., and titrated with 0.1N Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> indicated an enol content of 62.9%, after 8 weeks 25.6%. II (25 g.) in 100 cc. 5% alc. HCl refluxed 24 hrs. gave 24 g. 2-ethoxy-3,5-dicarbethoxytetrahydrofuran (XII), b<sub>0.1</sub> 93-5.degree., n<sub>22D</sub> 1.4412. XII (24 g.) and 3 drops concd. H<sub>2</sub>SO<sub>4</sub> heated about 3 hrs. at 145-50.degree. gave di-Et ester (XIII) of 3,5-dicarboxy-4,5-dihydrofuran (XIV), b<sub>0.1</sub> 101-10.degree., n<sub>22D</sub> 1.4659. XIII (5 g.) and 4 g. KOH in 30 cc. H<sub>2</sub>O heated 0.5 hr. on the water bath, cooled, acidified, and extd. with EtOAc yielded 2.9 g. XIV, m. 179-80.degree. (EtOAc). II (50 g.) treated dropwise at 0.degree. with 0.55 g. K in 20 cc. Me<sub>3</sub>COH and then during 0.5 hr. with 19 g. IV, the mixt. kept 10 hrs. at 20.degree., dild. with 500 cc. Et<sub>2</sub>O, acidified with 0.84 g. AcOH, and worked up yielded 60 g. AcCH<sub>2</sub>CH<sub>2</sub>C(CHO).CO.O.CH(CO<sub>2</sub>Et).CH<sub>2</sub> (XV), b<sub>0.1</sub> 185-90.degree., n<sub>22D</sub> 1.4815. XV (60 g.) in 250 cc. C<sub>6</sub>H<sub>6</sub> refluxed 25 hrs. with 3 cc. piperidine acetate and 3 cc. AcOH with **azeotropic** removal of 3.5 cc. H<sub>2</sub>O, evapd., and the residue worked up with Et<sub>2</sub>O yielded 38 g. 1-carboxy-2-cyclohexen-4-one-1-lactic acid Et ester **lactone** (XVI), b<sub>0.1</sub> 175-80.degree., n<sub>22D</sub> 1.5110, which on prolonged standing deposited about 15% cryst. XVI, m. 49-50.degree.. Oily XVI (6 g.) in 150 cc. MeOH hydrogenated 2 hrs. over 5% Pd-C gave 5.6 g. cyclohexanone analog (XVII) of XVI, b<sub>0.1</sub> 170-5.degree., n<sub>22D</sub> 1.4888, m. 75-6.degree.. Cryst. XVI (1 g.) gave similarly 950 mg. XVII. EtO<sub>2</sub>CCO(CH<sub>2</sub>)<sub>2</sub>CO<sub>2</sub>Et (XVIII) (160 g.), 127.6 g. HC(OEt)<sub>3</sub>, 30.3 g. abs. EtOH, and 2.16 cc. concd. H<sub>2</sub>SO<sub>4</sub> kept about 20 hrs. at room temp., dild. with 300 cc. Et<sub>2</sub>O, and worked up gave 153 g. di-Et ketal (XIX) of XVIII, b<sub>0.01</sub> 88.degree., n<sub>25D</sub> 1.4305, contg. about 5% XVIII. XIX (50 g.) and 16 g. HCO<sub>2</sub>Et added dropwise with cooling to 22 g. NaH in 20% xylene and 70 cc. abs. Et<sub>2</sub>O, the mixt. stirred 3 hrs. with cooling, treated with 5 g. HCO<sub>2</sub>Et, stirred again 3 hrs., treated with 5 g. each HCO<sub>2</sub>Et and NaH suspension, kept overnight at 20.degree., and worked up gave 46 g. III. III (26 g.), 20 cc. dry C<sub>6</sub>H<sub>6</sub>, and 600 mg. K in 10 cc. Me<sub>3</sub>COH treated dropwise at 0.degree. with 6 g. IV, the mixt. stirred several hrs. at 0-10.degree., kept at 20.degree. overnight, and worked up yielded 21.3 g. crude Ac(CH<sub>2</sub>)<sub>2</sub>C(CHO)(CO<sub>2</sub>Et)CH<sub>2</sub>C(OEt)<sub>2</sub>CO<sub>2</sub>Et (XX). Crude XX (20 g.), 1 g. piperidine acetate, and 1 cc. AcOH in 40 cc. C<sub>6</sub>H<sub>6</sub> refluxed 5 hrs. with the **azeotropic** removal of H<sub>2</sub>O, dild. with 100 cc. Et<sub>2</sub>O, and worked up gave 14.1 g. (crude) 1-carbethoxy-2-cyclohexen-4-

one-1-pyruvic acid Et ester di-Et ketal, b0.01 135-40.degree., n25D 1.4620. The ultraviolet absorption spectra of oily and solid XV were recorded.

CC 10D (Organic Chemistry: Alicyclic Compounds)

IT Ultraviolet and visible, spectra

(of 2-formyl-4-hydroxy-2-(3-oxobutyl)glutaric acid .gamma.-lactone Et ester)

IT 2931-38-6, 2-Cyclohexene-1-propionic acid, 1-carboxy-.alpha.,.alpha.-diethoxy-4-oxo-, diethyl ester 3097-73-2, Glutaric acid, 2-oxo-, diethyl ester, di-Et acetal 5965-53-7, Glutaric acid, 2-oxo-, diethyl ester 67133-08-8, 2-Cyclohexene-1-lactic acid, 1-carboxy-4-oxo-, .gamma.-lactone, Et ester 82977-45-5, Butyric acid, 4-(chloroformyl)-4-hydroxy-, .gamma.-lactone 99173-67-8, 2,4-Furandicarboxylic acid, 2,3-dihydro-, diethyl ester 100258-06-8, Cyclohexanelactic acid, 1-carboxy-4-oxo-, .gamma.-lactone, Et ester 100258-06-8, 2-Oxaspiro[4.5]decane-3-carboxylic acid, 1,8-dioxo-, ethyl ester 100258-26-2, Glutaric acid, 2-formyl-4-hydroxy-2-(3-oxobutyl)-, .gamma.-lactone, Et ester 100316-09-4, 2,4-Furandicarboxylic acid, 5-ethoxytetrahydro-, diethyl ester 100703-78-4, 2,4-Furandicarboxylic acid, 2,3-dihydro- 102154-93-8, Succinic acid, 2-formyl-2-(3-oxobutyl)-, diethyl ester 106164-15-2, 2-Furoic acid, 4-formyl-2,3-dihydro-5-hydroxy-, ethyl ester 108487-86-1, Glutaric acid, 2-formyl-4-hydroxy-, .gamma.-lactone, Et ester 109512-89-2, Glutaric acid, 2-formyl-4-oxo-, diethyl ester, 4-(di-Et acetal) 111530-53-1, Glutaric acid, 2,2-diethoxy-4-formyl-4-(3-oxobutyl)-, diethyl ester 111530-53-1, Glutaric acid, 2-formyl-4-oxo-2-(3-oxobutyl)-, diethyl ester, 4-(di-Et acetal)  
(prepn. of)

L35 ANSWER 6 OF 20 HCA COPYRIGHT 2005 ACS on STN

54:28371 Original Reference No. 54:5499i,5500a-i The synthesis of a second (stereoisomeric) tetrahydroprephenic acid and its steric assignment. Plieninger, Hans; Keilich, Gunda (Univ. Heidelberg, Germany). Chemische Berichte, 92, 2897-901 (Unavailable) 1959. CODEN: CHBEAM. ISSN: 0009-2940. OTHER SOURCES: CASREACT 54:28371.

GI For diagram(s), see printed CA Issue.

AB From the mother liquors of 4-benzyloxy-1-cyanocyclohexane-1-acetonitrile (I), m. 135-6.degree., was isolated a stereoisomer (II), m. 55-7.degree.. The configurations III and IV were established for the 2 tetrahydroprephenic acids from I and II, resp. The mother liquors from I evapd. in vacuo, and the dark residue recrystd. with C from hot EtOH gave I; the filtrate from the I cooled to 0.degree., filtered again from more I, and concd. further gave II, needles, m. 55-7.degree. (aq. MeOH). II (25.4 g.), 60 g. KOH, 85 cc. H2O, and 40 cc. EtOH refluxed 50-60 hrs., cooled, poured into 500 cc. cold H2O, acidified with cooling with concd. HCl to pH

1, kept 4 hrs. at 0.degree., and filtered gave 27.6 g. 4-benzyloxy-1-carboxycyclohexane-1-acetic acid (V), needles, m. 139-41.degree. (H<sub>2</sub>O). The isomer of V, m. 120-5.degree., was obtained similarly from I. V (5 g.) in 100 cc. MeOH hydrogenated at 20.degree./760 mm. over 5% Pd-C, filtered, evapd., and the residue boiled with C<sub>6</sub>H<sub>6</sub> yielded 2.7 g. 4-OH analog (VI) of V, cryst. powder, m. 170-4.degree.. The isomer (VII) of VI m. 155-62.degree.. VI (6 g.) in 50 cc. glacial AcOH treated dropwise with stirring during 0.5 hr. at 15-20.degree. with 4 g. K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, 4.8 cc. concd. H<sub>2</sub>SO<sub>4</sub>, and 25 cc. H<sub>2</sub>O, kept 2 hrs. with cooling and 12 hrs. at room temp., filtered, the residue washed with H<sub>2</sub>O, the combined filtrates extd. continuously with Et<sub>2</sub>O, the Et<sub>2</sub>O soln. worked up, and the residue ground with Et<sub>2</sub>O and washed with cold Et<sub>2</sub>O gave 3.6 g. 4-oxo-1-carboxycyclohexane-1-acetic acid, m. 161-5.degree.. VI (1.01 g.) in 50 cc. MeOH treated with cooling with 50 mg. AcCl, refrigerated several days, evapd. in vacuo, and the residual sirup cooled and triturated with C<sub>6</sub>H<sub>6</sub> yielded 905 mg. Me ester (VIII) of VI, m. 94.5-96.degree. (C<sub>6</sub>H<sub>6</sub>). VIII (2.16 g.) and 500 mg. p-MeC<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>H in 200 cc. dry C<sub>6</sub>H<sub>6</sub> refluxed 10-12 hrs. with the **azeotropic** removal of the H<sub>2</sub>O, filtered hot, cooled, and dild. with petr. ether gave the **lactone** (IX) of VI, m. 241-4.5.degree. (aq. EtOH or aq. AcOH), which was also obtained similarly from VI. VIII (1.08 g.) and 350 mg. N<sub>2</sub>H<sub>4</sub>.H<sub>2</sub>O heated 1-2 hrs. in a water bath and cooled yielded 968.1 mg. hydrazide of VI, m. 138-9.5.degree. (EtOH-Et<sub>2</sub>O), also obtained from IX in the same manner. VI (1 g.) in 25 cc. Ac<sub>2</sub>O and 5 cc. glacial AcOH refluxed 2 hrs. and evapd. gave 1.08 g. 4-acetoxy-1-carboxycyclohexane-1-acetic acid 1-anhydride (X), m. 118-20.degree. (C<sub>6</sub>H<sub>6</sub>-petr. ether). VII (2.02 g.) in 50 cc. MeOH treated with cooling with 50 mg. AcCl, kept several days, evapd., and the residue **distd.** gave 1.5 g. Me ester (XI) of XII, b<sub>0.01</sub> 77-9.degree., m. 36.5-38.degree.. VII (3.03 g.) and 500 mg. p-MeC<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>H in 250 cc. C<sub>6</sub>H<sub>6</sub> refluxed 10-12 hrs. with the **azeotropic** removal of H<sub>2</sub>O, cooled, filtered, dild. with ligroine (b. 60-70.degree.) to turbidity, and refrigerated several hrs. gave 2.3 g. XII, m. 135-6.5.degree.. XII esterified with HCl-MeOH gave XI, m. 36-8.degree.. Similarly was prepd. the higher melting isomer, m. 158.5-61.degree. (C<sub>6</sub>H<sub>6</sub>-petr. ether), of X in 86.8% yield. By the methods described previously [Ber. 90, 1973(1957)] for the isomers were prepd. the following compds.: Et (1-cyano-4-benzyloxy-1-cyclohexyl)cyanopyruvate K enolate, 68%, m. 185-95.degree.; enol **lactone** of Et (1-carboxy-4-benzyloxy-1-cyclohexyl)cyanopyruvate, m. 85-6.degree. (EtOH); 2,4-dinitrophenylhydrazone of (1-carboxy-4-benzyloxy-1-cyclohexyl)pyruvic acid, m. 212-15.degree. (aq. EtOH); tetrahydroprephenic acid 2,4-dinitrophenylhydrazone, m. 232-5.5.degree. (aq. EtOH), 78%.

CC 10D (Organic Chemistry: Alicyclic Compounds)  
IT 2-Oxaspiro[4.5]dec-3-ene-1,3-dione, 8-hydroxy-, acetate

- 2-Oxaspiro[4.5]dec-3-ene-3-carboxylic acid, 8-(benzyloxy)-4-cyano-1-oxo-, ethyl ester  
 2-Oxaspiro[4.5]**decane**-3-carboxylic acid,  
 3-(benzyloxy)-4-cyano-1-oxo-, ethyl ester  
 Cyclohexanepyruvic acid 4-(benzyloxy)-1-carboxy-,  
 4-(benzyloxy)-.beta.,1-dicyano-, ethyl ester, K deriv.  
 IT 70909-78-3, 2-Oxabicyclo[2.2.2]octane-4-acetic acid, 3-oxo-  
 70909-80-7, 2-Oxabicyclo[3.2.2]nonane-5-carboxylic acid, 3-oxo-  
 98954-74-6, Cyclohexaneacetic acid, 1-carboxy-4-oxo- 99173-34-9,  
 2-Oxabicyclo[2.2.2]octane-4-acetic acid, 3-oxo-, methyl ester  
 102012-93-1, Cyclohexaneacrylic acid, 4-(benzyloxy)-1-carboxy-.beta.-  
 cyano-.alpha.-hydroxy-, .gamma.-**lactone**, Et ester  
 102656-77-9, Cyclohexanepyruvic acid 4-(benzyloxy)-1-carboxy-,  
 (2,4-dinitrophenyl)hydrazone  
 (prepn. of)  
 IT 100145-33-3, Cyclohexaneacetic acid, 1-carboxy-4-hydroxy-  
 (stereoisomers, and .epsilon.-**lactone** and anhydride and  
 other derivs.)

L35 ANSWER 7 OF 20 HCA COPYRIGHT 2005 ACS on STN

54:16645 Original Reference No. 54:3265d-i,3266a-i,3267a-g The reaction of 2-substituted cyclohexanones with organometallic compounds. McElvain, S. M.; Clampitt, Rodney B. (Univ. of Wisconsin, Madison). Journal of the American Chemical Society, 81, 5590-8 (Unavailable) 1959. CODEN: JACSAT. ISSN: 0002-7863. OTHER SOURCES: CASREACT 54:16645.

AB The reactions of a series of 2-substituted cyclohexanones with PhMgBr (I) and PhLi were investigated. While a EtO<sub>2</sub>CCH<sub>2</sub> or a EtO<sub>2</sub>C(CH<sub>2</sub>)<sub>2</sub> group in the 2-position yielded as the major reaction product the metal enolate of the original ketone, a Me<sub>2</sub>NCH<sub>2</sub> group led to the normal addn. of the organometallic compd. to the oxo function. If the amino function was sepd. from the ring by 2 or 3 CH<sub>2</sub> groups, the enolization reaction was the main or only reaction with I; however, these substituents did not interfere with the normal addn. of PhLi to the ketone. Nonpolar alkyl groups in the 2-position led with I and with PhLi to the normal addn. products. A rationalization of these results was proposed. Et 1-carbethoxy-2-oxocyclohexaneacetate (100 g.), 150 cc. concd. HCl, and 150 cc. glacial AcOH refluxed 17 hrs., evapd., and the residue reesterified with EtOH yielded 54.6 g. Et 2-oxocyclohexaneacetate (II), b0.10 79-80.degree., n<sub>25D</sub> 1.4572; 2,4-dinitrophenylhydrazone m. 128-9.degree. (EtOH); semicarbazone m. 196-6.5.degree. (aq. EtOH). Et 2-oxocyclohexanecarboxylate (III) (85.1 g.) and 400 cc. dry C<sub>6</sub>H<sub>6</sub> **distd.** to remove 200 cc. C<sub>6</sub>H<sub>6</sub>, the residual mixt. treated with 0.6 g. NaH, followed by 50 g. CH<sub>2</sub>:CHCO<sub>2</sub>Et contg. 0.25% hydroquinone, kept 3 days at room temp., heated 1 hr. on the steam bath, washed, dried, and **distd.** gave 117.3 g. 1-CO<sub>2</sub>Et deriv. (IV) of Et 2-oxo-cyclohexanepropionate (V), b0.12-0.22

123-32.degree., n25D 1.4622. IV (229.8 g.) in 1:1 concd. HCl-glacial AcOH hydrolyzed and decarboxylated and the product reesterified with EtOH gave 141.3 g. V, b0.13-0.15 96-100.degree., n25D 1.4622; 2,4-dinitrophenylhydrazone m. 89-91.degree. (EtOH). II (25.0 g.), 9.3 g. (CH<sub>2</sub>OH)<sub>2</sub>, and 50 mg. p-MeC<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>H in 30 cc. C<sub>6</sub>H<sub>6</sub> refluxed 3 hrs. (with the **azeotropic** removal of H<sub>2</sub>O) and worked up gave 26.9 g. Et 2,2-ethylenedioxcyclohexaneacetate (VI), b0.12 87-90.degree., n25D 1.4645. VI (15.0 g.), 15 cc. Me<sub>2</sub>NH, and 0.5 cc. H<sub>2</sub>O heated 12 hrs. at 175.degree. in a steel bomb gave 1.4 g. forerun, b0.06 87-113.degree., and 12.4 g. N,N-dimethyl-2,2-ethylenedioxcyclohexaneacetamide (VII), b0.05 112.degree., n25D 1.4922. VII (10.0 g.) in 75 cc. dry Et<sub>2</sub>O added during 2 hrs. to 1.67 g. LiAlH<sub>4</sub> in 100 cc. dry Et<sub>2</sub>O, stirred 1.5 hrs. decompd. with 75 cc. 10% aq. KOH, and worked up in the usual manner yielded 6.5 g. 2-(2-dimethylaminoethyl)cyclohexanone (VIII), b10 106-9.degree., n25D 1.4651; picrate, m. 119-20.degree. (EtOH). V was converted similarly in 83% yield to Et 2,2-ethylenedioxcyclohexanepropionate, b0.15 99-101.degree., n25D 1.4663, and this further in 92% yield to N,N-dimethyl-2,2-ethylenedioxcyclohexanepropionate (IX), b0.06 128.degree., n25D 1.4934. IX reduced and hydrolyzed in the usual manner yielded 94% 2-(3-dimethylaminopropyl)-cyclohexanone (X), b0.15 71.degree., n25D 1.4656; picrate m. 107-8.degree. (MeOH). III (34.0 g.) added dropwise during 1 hr. to 4.8 g. NaH in 150 cc. dry xylene under N, refluxed 1 hr., treated with 33.2 g. iso-AmBr, refluxed 24 hrs., cooled, and treated during 10 min. with 90 cc. cold 10% H<sub>2</sub>SO<sub>4</sub>, and the org. layer washed, dried, and **distd**. gave 32.0 g. crude product which, shaken 15 min. with 5% aq. NaOH and redistd., yielded pure Et 1-isoamyl-2-oxocyclohexanecarboxylate (XI), b0.22 93-4.degree., n25D 1.4558. XI (25.0 g.) in 100 cc. 30% H<sub>2</sub>SO<sub>4</sub> and 200 cc. glacial AcOH refluxed 24 hrs., cooled to room temp., treated with solid Na<sub>2</sub>CO<sub>3</sub> in portions, and dild. with H<sub>2</sub>O to soln., the aq. layer extd. with Et<sub>2</sub>O, and the combined org. layer and Et<sub>2</sub>O ext. worked up yielded 11.6 g. 2-isoamylcyclohexanone, b0.3 58.degree., n25D 1.4529; 2,4-dinitrophenylhydrazone, orange plates, m. 123-5.degree. (aq. EtOH); semicarbazone, plates, m. 152-4.degree. (aq. EtOH). Isohexyl bromide, b. 146-8.degree., n25D 1.4410, d<sub>25</sub> 1.1342, was converted similarly in 67% yield to Et 1-isohexyl-2-oxocyclohexanecarboxylate, b0.35 113-15.degree., n25D 1.4564, which hydrolyzed and decarboxylated gave 73% 2-isohexylcyclohexanone (XII), b0.22 70.degree., n25D 1.4541; 2,4-dinitrophenylhydrazone, orange needles, m. 125-6.degree. (EtOH); semicarbazone m. 143-5.degree. (aq. EtOH). II (18.42 g.) in 50 cc. dry Et<sub>2</sub>O treated under N with 67.2 cc. 1.49N I with stirring during 1.5 hrs., refluxed 0.5 hr., cooled, and treated dropwise during 10 min. with 75 cc. 10% HCl, and the product isolated in the usual manner and **distd.** yielded 38.6 g. unchanged II and 28.5% **lactone** (XIII) of 2-hydroxy-2-phenylcyclohexaneacetic acid (XIV), needles, m. 60-1.degree.. XIII hydrolyzed with an equiv. of

aq. alkali, the mixt. concd. and acidified, and the product isolated with Et<sub>2</sub>O yielded XIV, m. 127-8.degree. (C<sub>6</sub>H<sub>6</sub>-ligroine, b. 60-8.degree.). XIII (2.16 g.) in 10 cc. dry Et<sub>2</sub>O added dropwise to I (from 0.56 g. Mg and 3.62 g. PhBr in 17 cc. dry Et<sub>2</sub>O), refluxed 0.5 hr., treated dropwise with 15 cc. 10% HCl, and the product isolated in the usual manner gave 2.13 g. 2-(2,2-diphenyl-2-hydroxyethyl)-1-phenylcyclohexanol, m. 129.5-30.5.degree. (cyclohexane). V (19.86 g.) treated in the usual manner with 68.2 cc. 1.47N I in Et<sub>2</sub>O and worked up gave 37% unchanged V and 38% 2-hydroxy-2-phenylcyclohexanepropionic acid **lactone** (XV), needles, m. 74-5.5.degree. (petr. ether). V (19.82 g.) treated in the usual manner with 94 cc. 1.064N PhLi in Et<sub>2</sub>O, decompd. with H<sub>2</sub>O, and the org. layer worked up gave 11.07 g. unchanged V and 3.26 g. XV, b0.20 153-60.degree., and left a considerable amt. of glassy residue. I from 1.88 g. Mg and 12.15 g. PhBr in 50 cc. dry Et<sub>2</sub>O treated during 45 min. under N with 10.00 g. 2-dimethylaminomethylcyclohexanone (XVI), b10 91-4.degree., n<sub>25D</sub> 1.4633 (XVI.HCl, m. 151-2.5.degree.) in 50 cc. dry Et<sub>2</sub>O, refluxed 0.5 hr. on the steam bath, decompd. with aq. NH<sub>4</sub>Cl, and worked up in the usual manner yielded 0.76 g. unchanged XVI and 10.01 g. 2-dimethylaminomethyl-1-aminomethyl-1-phenylcyclohexanol (XVII), b0.07 100.degree., n<sub>25D</sub> 1.5299 (apparently a mixt. of stereoisomers). Dry HCl in Et<sub>2</sub>O added dropwise to 10.0 g. XVII and filtered gave a solid, m. 166-90.degree., which fractionally crystd. from Me<sub>2</sub>CO gave 5.2 g. XVII.HCl, m. 188-9.degree., and 1.4 g. XVII.HCl, m. 189-91.degree.. XVII.HCl (3.00 g.), m. 188-9.degree., in 10 cc. H<sub>2</sub>O treated with 1 g. KOH in 5 cc. H<sub>2</sub>O, allowed to stand, and filtered gave 2.56 g. XVII, m. 54-6.degree.. The isomeric XVII.HCl, m. 189-91.degree., gave similarly a noncrystallizable oil. XVI (10.00 g.) in 50 cc. dry Et<sub>2</sub>O added dropwise during 1 hr. to PhLi (from 1.12 g. Li and 10.6 g. PhBr in 35 cc. dry C<sub>6</sub>H<sub>6</sub>), refluxed 0.5 hr., decompd. with 25 cc. H<sub>2</sub>O and worked up in the usual manner gave 1.09 g. unchanged XVI and 11.26 g. XVII, b0.15 103-9.degree.. VIII (10.00 g.) in Et<sub>2</sub>O added to I from 11.12 g. PhBr and 1.72 g. Mg and processed in the usual manner gave 50% unchanged VIII and 5.95 g. 2-(2-dimethylaminoethyl)-1-phenylcyclohexanol (XVIII), m. 61-70.degree., b0.07, 106-30.degree., which, recrystd. from aq. MeOH, gave 50% XVIII, m. 71-2.degree.; the remainder of XVIII was recovered in cryst. form from the mother liquor, but melted over a wide range; XVIII was evidently a mixt. of diastereoisomers with 1 isomer predominating. XVIII, m. 72.degree., treated with HCl in Et<sub>2</sub>O gave XVIII.HCl, m. 200-2.degree. (decompn.) (EtOH-EtOAc). The mixed isomeric XVII treated with HCl-Et<sub>2</sub>O gave 60% prisms, m. 200-2.degree. (decompn.); the remainder of the XVIII.HCl melted at 195-200.degree. (decompn.). VIII (10.00 g.) treated in the usual manner with PhLi (from 1.03 g. Li and 9.74 g. PhBr) gave 1.75 g. unchanged VIII and 10.52 g. XVIII, b0.05 106-9.degree.; a 7.00 g. sample of the XVIII recrystd. from aq. MeOH gave 3.93 g. XVIII,

needles, m. 70-2.degree.; the remainder of the XVIII did not crystallize. X (7.50 g.) treated in the usual manner with I (from 1.21 g. Mg and 7.70 g. PhBr) gave 6.65 g. unchanged X, b0.1 70-1.degree., and 0.70 g. dark gummy residue. X (7.30 g.) in 35 cc. dry Et2O added to I (from 1.21 g. Mg and 7.70 g. PhBr in Et2O), refluxed 0.5 hr., allowed to settle, filtered under N, the residue washed with Et2O, the combined filtrates kept 4 days under N, refluxed 4 hrs., cooled, filtered, and the residue hydrolyzed yielded 0.15 g. unchanged X; the Et2O filtrate fractionated gave 1.31 g. C6H6, b. 77.degree.. n25D 1.4817 [m-C6H4(NO2)2, m. 88-9.degree.]. The original filter residue suspended in 50 cc. Et2O, decompd. with excess satd. aq. NH4Cl, washed with Et2O, satd. with solid K2CO3, extd. with Et2O, and the ext. worked up yielded 5.95 g. X, b0.15 71-3.degree., n25D 1.4657, and 0.33 g. tarry residue. X (10.00 g.) added to PhLi (from 0.96 g. Li and 9.0 g. PhBr in Et2O) and worked up in the usual manner gave 1.45 g. unchanged X and 10.15 g. 2-(3-dimethylaminopropyl)-1-phenylcyclohexanol (XIX), m. 104.5-106.degree. (ligroine, b. 60-8.degree.); XIX.HCl m. 206-8.degree. (decompn.) (EtOH-EtOAc). XI (5.00 g.) in 30 cc. dry Et2O added under N to I (from 0.87 g. Mg and 5.61 g. PhBr in 30 cc. dry Et2O) with stirring during 1 hr., refluxed 0.5 hr., decompd. with aq. NH4Cl, and the product isolated in the usual manner gave 4.8% unchanged XI and 6.00 g. 2-(3-methylbutyl)-1-phenylcyclohexanol (XX), b0.30 12.degree., n25D 1.5162. XI added with stirring to PhLi (from 0.52 g. Li and 4.91 g. PhBr in 30 cc. Et2O) under N, refluxed 0.5 hr., cooled to room temp., decompd. with 20 cc. H2O, and worked up in the usual manner gave 0.70 g. unchanged XI and 5.89 g. XX, b0.15 113-14.degree., n25D 1.5159. XII (5.00 g.) added to I (from 0.80 g. Mg and 5.17 g. PhBr) and worked up gave 0.67 g. unchanged XII and 80% 2-(4-methylpentyl)-1-phenylcyclohexanol (XXI), b0.08 120.degree., n25D 1.5142. XVII (2.00 g.), m. 54-6.degree., 0.96 g. EtCO2Na, and 20 cc. (EtCO)2O heated 8 hrs. on the steam bath, poured into 50 cc. H2O, allowed to stand, satd. with K2CO3, extd. with Et2O, and the ext. worked up gave 2.44 g. 2-dimethylaminomethyl-1-phenyl-1-propionyloxycyclohexane-HCl (XXII.HCl), m. 183-5.degree. (decompn.) (EtOH-EtOAc). Mixed isomeric XVII (13.4 g.) gave similarly 16.3 g. XXII.HCl, m. 170-81.degree., which, fractionally crystd. from EtOH-EtOAc, yielded 9.9 g. prisms, m. 183-5.degree. (decompn.), and 1.89 g. needles, m. 180-2.degree. (decompn.). XVIII (1 g.), m. 71-2.degree., 0.48 g. EtCO2Na, and 25 cc. (EtCO)2O heated 24 hrs. with stirring at 115-20.degree., cooled to room temp., poured into 50 cc. H2O, satd. with K2CO3, and extd. with Et2O yielded 0.76 g. 2-(2-dimethylaminoethyl) analog (XXIII) of XXII.HCl, plates, m. 181-2.degree. (decompn.) (EtOAc). XVIII.HCl in (EtCO)2O heated 24 hrs. at 115-20.degree. gave 46% XXII.HCl. XIX heated with EtCO2Na and (EtCO)2O 24 hrs. at 115.degree. or at 125.degree., treated with EtCOCl in C6H6, or treated in Et2O with 1 equiv. PhLi,



followed by EtCOCl gave in all cases only XIX.HCl. XIX.HCl in (EtCO)<sub>2</sub>O heated 24 hrs. at 135-40.degree. gave 9.6% 1-(or 6) (3-dimethylaminopropyl)-2(or 1)-phenylcyclohexene-HCl, m. 173-5.degree.. XXI (3.0 g.), 1.1 g. EtCO<sub>2</sub>Na, and 30 cc. (EtCO)<sub>2</sub>CO heated 24 hrs. at 125.degree. with stirring, evapd. in vacuo at 100.degree., the residue dissolved in 40 cc. dry Et<sub>2</sub>O, filtered, and the filtrate evapd. yielded 2.0 g. unchanged XXI, b0.1 121-4.degree., n<sub>D</sub><sup>25</sup> 1.5130, and an undistillable brown gum. XXII.HCl and XXIII.HCl did not show any analgesic activity, but exhibited signs of neurotoxicity at 80 mg./kg. in rats.

CC 10D (Organic Chemistry: Alicyclic Compounds)

IT 4095-02-7, Cyclohexanepropionic acid, 2-oxo-, ethyl ester  
 4137-49-9, Coumarin, octahydro-8a-phenyl- 21405-66-3,  
 Cyclohexaneacetic acid, 2-hydroxy-2-phenyl-, .gamma.-lactone  
 21405-67-4, Cyclohexaneacetic acid, 2-hydroxy-2-phenyl-  
 33050-94-1, 1,4-Dioxaspiro[4.5]**decane**-6-propionic acid,  
 ethyl ester 57133-55-8, 1,4-Dioxaspiro[4.5]**decane**  
 -6-acetic acid, ethyl ester 93437-99-1, Cyclohexanepropionic acid,  
 2-oxo-, (2,4-dinitrophenyl)hydrazine 93865-05-5,  
 Cyclohexanepropionic acid, 1-carboxy-2-oxo-, diethyl ester  
 101099-19-8, Cyclohexanecarboxylic acid, 1-isopentyl-2-oxo-, ethyl  
 ester 101740-76-5, Cyclohexanol, 2-isopentyl-1-phenyl-  
 103212-25-5, Cyclohexaneethanol, 2-hydroxy-.alpha.,.alpha.,2-  
 triphenyl- 103856-94-6, Cyclohexanone, 2-(3-dimethylaminopropyl)-  
 105789-28-4, 1,4-Dioxaspiro[4.5]**decane**-6-acetamide,  
 N,N-dimethyl- 107328-57-4, Cyclohexanone, 2-(3-  
 dimethylaminopropyl)-, picrate 109252-88-2, Cyclohexanol,  
 2-(3-dimethylaminopropyl)-1-phenyl-, hydrochloride 109252-89-3,  
 Cyclohexanol, 2-(3-dimethylaminopropyl)-1-phenyl- 109449-18-5,  
 Cyclohexanecarboxylic acid, 1-isohexyl-2-oxo-, ethyl ester  
 109642-07-1, Cyclohexanol, 2-isohexyl-1-phenyl- 111438-26-7,  
 1-Cyclohexene-1-propylamine, N,N-dimethyl-2-phenyl-(?),  
 hydrochloride 111438-27-8, 2-Cyclohexene-1-propylamine,  
 N,N-dimethyl-2-phenyl-(?), hydrochloride 131081-71-5,  
 1,4-Dioxaspiro[4.5]**decane**-6-propionamide, N,N-dimethyl-  
 (prep. of)

L35 ANSWER 8 OF 20 HCA COPYRIGHT 2005 ACS on STN

54:2394 Original Reference No. 54:606b-i,607a-e Syntheses in the series of the aromatic erythrina alkaloids. I. Synthesis of racemic trans-15,16-dimethoxy-erythrinan. Mondon, Albert (Univ. Kiel, Germany). Chemische Berichte, 92, 1461-71 (Unavailable) 1959. CODEN: CHBEAM. ISSN: 0009-2940.

GI For diagram(s), see printed CA Issue.

AB Cyclohexanone (100 g.) and 160 g. pyrrolidine **azeotroped** with 2 g. Dowex-50 and 300 cc. dry C<sub>6</sub>H<sub>6</sub>, and the dried soln. **distd.** yielded 142 g. enamine (I), b<sub>10</sub> 105.degree., n<sub>D</sub><sup>20</sup> 1.5201. I (100 g.) and 90 cc. abs. MeOH treated during 15 min. with

stirring with 160 g. BrCH<sub>2</sub>CO<sub>2</sub>Et while removing a portion of the MeOH by **distn.**, the remainder of the MeOH **distd.** during 50 min., the hot residue dild. with 100 cc. H<sub>2</sub>O, stirred 1 hr. at 70.degree., cooled, satd. with NaCl, and the product isolated with Et<sub>2</sub>O yielded 72 g. Et 2-oxocyclohexylacetate (II), b<sub>10</sub> 125-6.degree., n<sub>20D</sub> 1.4599; 2,4-dinitrophenylhydrazone, orange needles, m. 130-1.degree. (EtOH). Ph(CH<sub>2</sub>)<sub>2</sub>NH<sub>2</sub> (2.8 g.), 4 g. II, and 40 g. polyphosphoric acid heated 20 hrs. at 100.degree., poured into H<sub>2</sub>O, and extd. with Et<sub>2</sub>O, the ext. washed, dried, and evapd., and the residue (2.9 g.) chromatographed on Al<sub>2</sub>O<sub>3</sub> gave 2.3 g. **lactone** III, b<sub>10</sub> 140.degree. (bath), and 0.24 g. erythrinan-8-one (IV), m. 83-5.degree. (pentane-Et<sub>2</sub>O). IV (150 mg.) refluxed 4 hrs. with 80 rag. LiAlH<sub>4</sub> in 10 cc. dry Et<sub>2</sub>O gave erythrinan (V), b<sub>0.03</sub> 110.degree. (bath); picrate, m. 180-1.degree. (90% EtOH); V.MeI, m. 210.degree. (Me<sub>2</sub>CO). II (70 g.), 22 g. (CH<sub>2</sub>OH)<sub>2</sub>, 300 cc. dry C<sub>6</sub>H<sub>6</sub>, and 3 g. Dowex-50 heated 14 hrs. at 120-5.degree., filtered, and **distd.** gave 76.2 g. ethylene ketal (VI) of II, b<sub>10</sub> 136-8.degree., n<sub>20D</sub> 1.4658. VI (76.2 g.), 30 g. KOH, 80 cc. EtOH, and 80 cc. H<sub>2</sub>O heated 2 hrs. on the water bath, cooled to 0.degree., treated with 71 cc. cold 6N H<sub>2</sub>SO<sub>4</sub>, satd. with NaCl, and extd. with Et<sub>2</sub>O yielded nearly 100% 2-oxocyclohexylacetic acid ethylene ketal (VII), b<sub>0.02</sub> 123.degree., n<sub>20D</sub> 1.4829; 2,4-dinitrophenylhydrazone, orange needles, m. 203.degree. (hot C<sub>6</sub>H<sub>6</sub>). VII with 2,4-(O<sub>2</sub>N)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NHNH<sub>2</sub> in MeOH-H<sub>2</sub>SO<sub>4</sub> yielded the deriv., m. 138.degree., of the Me ester of VII. VII (10 g.), 10.5 g. Et<sub>3</sub>N, and 9.55 cc. ClCH<sub>2</sub>CN cooled, kept 45 min. at room temp., heated 0.5 hr. at 70.degree., and **distd.** gave 94% NCCH<sub>2</sub> ester of VII, b<sub>0.04</sub> 130.degree. (bath), n<sub>20D</sub> 1.4475. VII (16.8 g.) and 15.2 g. homoveratrylamine (VIII) heated 20 hrs. at 180.degree., cooled, dissolved in CH<sub>2</sub>Cl<sub>2</sub>, washed, dried, and evapd., and the residual resin warmed with 50 cc. Et<sub>2</sub>O yielded 20.2 g. N-[2-(3,4-dimethoxyphenyl)ethyl]-2-oxo-cyclohexylacetamide ethylene ketal (IX), m. 123.degree. (C<sub>6</sub>H<sub>6</sub>-petr. ether); 2,4-dinitrophenylhydrazone, pale yellow needles, m. 205.degree.. NCCH<sub>2</sub> ester (4.18 g.) of IX, 3.16 g. VIII, and 17.5 cc. EtOAc heated 20 hrs. at 60.degree. and **distd.** yielded 80% IX, m. 123.degree.. VII (2 g.) and 2g. VIII in 10 cc. CH<sub>2</sub>Cl<sub>2</sub> treated with 2 g. N,N'-dicyclohexylcarbodiimide and filtered after 24 hrs. gave 0.83 g. N,N'-dicyclohexyl-urea; the filtrate washed, dried, and evapd., and the oily residue (4.2 g.) crystd. (aq. MeOH) gave the adduct X, m. 134.degree.; 2,4-dinitrophenylhydrazone, yellow, m. 254.degree. (MeOH). The mother liquor from X and 10 cc. dil. H<sub>3</sub>PO<sub>4</sub> heated 15 min. on the water bath, stirred 20 min. with cooling, and the neutral portion of the product isolated and digested with Et<sub>2</sub>O gave 0.8 g. N-[2-(3,4-dimethoxyphenyl)ethyl]-2-oxocyclohexylacetamide (XI), m. 116-17.degree. (C<sub>6</sub>H<sub>6</sub>-petr. ether); 2,4-dinitrophenylhydrazone, yellow needles m. 205.degree. (MeOH). The mother liquor from XI heated at 155.degree./12 mm. eliminated

with foaming a strong lacrimator, and the residue fractionally crystd. (petr. ether) gave a mixt. of 70:30 N-cyclohexyl derivs. of VII and of 2-cyclohexylacetic acid, m. 134.degree., and prisms, m. 124.degree.. IX (2 g.), 5 cc. C<sub>6</sub>H<sub>6</sub>, and 10 cc. dil. H<sub>3</sub>PO<sub>4</sub> shaken 10 hrs. at room temp. and extd. with C<sub>6</sub>H<sub>6</sub> gave 1.27 g. XI, m. 116-17.degree.. IX (19.35 g.), 7.6 g. VIII, and 2 g. Dowex-50 heated 5 hrs. at 150.degree. and then gradually during 5 hrs. to 190.degree., while removing a **distillate** of aq. (CH<sub>2</sub>OH)<sub>2</sub>, the residue cooled, kept at 120.degree./12 mm., and then **distd.**, and the viscous **distillate** (23.4 g.) dissolved in C<sub>6</sub>H<sub>6</sub> and dild. with petr. ether yielded 21 g. pure 15,16-dimethoxyerythrinan-8-one (XII), m. 117-18.degree.; the mother liquor chromatographed on Al<sub>2</sub>O<sub>3</sub> gave addnl. XII and a colorless, noncrystg. resin, apparently compd. XIII. IX (5 g.) and 0.1 g. cryst. H<sub>3</sub>PO<sub>4</sub> heated at 150.degree. until the elimination of (CH<sub>2</sub>OH)<sub>2</sub> and **distd.** gave 2.9 g. XII, m. 117-18.degree.. IX (5 g.) in 100 cc. C<sub>6</sub>H<sub>6</sub> refluxed 20 hrs. with 2 g. Dowex-50, filtered, and evapd. gave 2.81 g. XII. IX (5 g.), 6 cc. 85% H<sub>3</sub>PO<sub>4</sub>, 4 cc. H<sub>2</sub>O, and 10 cc. MeOH heated 1 hr. on the water bath and evapd. in vacuo, the residue dild. with H<sub>2</sub>O, and the product isolated with C<sub>6</sub>H<sub>6</sub> gave 3.2 g. XII. XI (2 g.) gave similarly 1.2 g. XII. IX (6 g.) and 0.9 g. LiAlH<sub>4</sub> refluxed 4 hrs. in 90 cc. tetrahydrofuran yielded 4.4 g. [2(3,4-dimethoxyphenyl)ethyl]-[2-(2-oxocyclohexyl)ethyl]amine ethylene ketal (XIV), b0.01 160.degree. (bath). XIV (2 g.) and 2 g. Dowex-60 heated 6 hrs. at 170.degree. and **distd.** gave only colorless oil, b0.1 170.degree. (bath). XIV (2 g.) and 10 g. polyphosphoric acid heated 10 hrs. at 100.degree. gave the same result. XII (10 g.) in 200 cc. tetrahydrofuran refluxed 4 hrs. with 5.6 g. LiAlH<sub>4</sub> yielded nearly 100% (+-)-trans-15,16-dimethoxyerythrinan (XV), b0.0001 110.degree. (bath); XV.HCl, m. 226.degree. (EtOH-Et<sub>2</sub>O); XV.HBr, m. 257.degree. (CHCl<sub>3</sub>-Me<sub>2</sub>CO); XV.HClO<sub>4</sub>, m. 250.degree. (MeOH); pierate of XV, m. 181.degree. (EtOH); XV.MeI, m. 200.degree. (Me<sub>2</sub>CO). XIV (11.5 g.) and 100 cc. 48% HBr heated 16 hrs. under N at 140.degree., concd., and filtered gave (+-)-trans-15,16-dihydroxyerythrinan-HBr (XVI.HBr), m. 283.degree. (decompn.) (48% HBr). Aq. XVI.HBr layered with Et<sub>2</sub>O and basified under N with dil. NH<sub>4</sub>OH and the Et<sub>2</sub>O layer worked up gave XVI, m. 180-3.degree. (C<sub>6</sub>H<sub>6</sub>); it gave with FeCl<sub>3</sub> in MeOH a deep green color; pierate of XVI, m. 208.degree. (70% EtOH).

CC 10H (Organic Chemistry: Alkaloids)

IT 4889-97-8, 1,4-Dioxaspiro[4.5]**decane**-6-acetic acid

27711-98-4, Erythrinan 27766-33-2, 1H-Indolo[7a,1-a]isoquinoline, 2,3,4,4a,5,6,8,9-octahydro-  
(and derivs.)

IT 1438-96-6, Cyclohexaneacetic acid, 2-oxo- 2387-23-7, Urea, 1,3-dicyclohexyl- 26775-04-2, 6H-Indolo[7a,1-a]isoquinolin-6-one, 1,2,3,4,4a,5,8,9-octahydro-11,12-dimethoxy- 101865-05-8, Cyclohexaneacetamide, N-(3,4-dimethoxyphenethyl)-2-oxo-

102666-68-2, Cyclohexaneacetamide, N-(3,4-dimethoxyphenethyl)-2-oxo-, (2,4-dinitrophenyl)hydrazone 103050-33-5, Urea, 1,3-dicyclohexyl-1-(2-oxocyclohexylacetyl)-, (2,4-dinitrophenyl)hydrazone 109642-65-1, 6H-Indolo[7a,1-a]isoquinolin-6-one, 1,2,3,4,4a,5,8,9-octahydro-13-hydroxy-12-methoxy-110053-05-9, 1,4-Dioxaspiro[4.5]**decane**-6-ethylamine, N-(3,4-dimethoxyphenethyl)- 110531-43-6, 1,4-Dioxaspiro[4.5]**decane**-6-acetamide, N-(3,4-dimethoxyphenethyl)- 114002-35-6, Urea, 1,3-dicyclohexyl-1-(1,4-dioxaspiro-[4.5]dec-6-ylacetyl)-  
(prepn. of)

L35 ANSWER 9 OF 20 HCA COPYRIGHT 2005 ACS on STN

53:62350 Original Reference No. 53:11269a-i,11270a Synthesis of hydroaromatic oxolactones. Rosenmund, Karl W.; Kositzke, Gustav (Univ. Kiel, Germany). Chemische Berichte, 92, 486-93 (Unavailable) 1959. CODEN: CHBEAM. ISSN: 0009-2940.

AB Na (1.2 g.) in 30 cc. abs. EtOH treated with 9 g. CH<sub>2</sub>(CO<sub>2</sub>Et)<sub>2</sub>, stirred until a homogeneous paste resulted, treated slowly dropwise with stirring with 10 g. 3-bromocyclohexene below 40.degree. during 15 min., concd. in vacuo, dild. with H<sub>2</sub>O, extd. with Et<sub>2</sub>O, and the ext. dried and **distd.** gave 11.7 g. di-Et ester (I) of 2-cyclohexenylmalonic acid (II), b<sub>12</sub> 149-50.degree.. I (11.3 g.), 7.8 g. KOH, and 7 cc. H<sub>2</sub>O heated 1 hr. on the water bath, cooled, washed with Et<sub>2</sub>O, acidified with 6N HCl, and filtered gave 7.5 g. II, needles, m. 166.degree. (Et<sub>2</sub>O). II (7.5 g.) heated 1 hr. at 170-80.degree. and **distd.** gave 5 g. 2-cyclohexenylacetic acid (III), b<sub>12</sub> 124-6.degree.. I (40 g.) in 200 cc. 100% HCO<sub>2</sub>H treated with stirring with 35 g. 30% H<sub>2</sub>O<sub>2</sub>, stirred 12 hrs. at 45.degree., kept at 20.degree. overnight, evapd. in vacuo, the residual oily diformate (IV) added with cooling to 40 g. KOH in 40 cc. H<sub>2</sub>O, cooled, poured into 150 cc. 1:3 hot HCl, extd. with EtOAc 6 hrs. in a Soxhlet app., and the ext. concd. to 50 cc. deposited 25 g. 2,3-dihydroxycyclohexylmalonic acid **lactone** (V), needles, m. 168-9.degree.. The crude IV from a similar run stirred into 300 cc. H<sub>2</sub>O, heated 1 hr. at 40.degree., extd. with EtOAc, and the ext. washed and **distd.** gave the Et ester of V, sirup, b<sub>0.2</sub> 165-8.degree.. V (6 g.) heated 1 hr. at 160.degree. and **distd.** yielded 4.5 g. 2,3-dihydroxycyclohexylacetic acid **lactone** (VI), b<sub>0.1</sub> 129-30.degree., b<sub>12</sub> 190-3.degree.. III (12.8 g.) in 77 cc. 100% HCO<sub>2</sub>H treated with stirring with 11 g. 30% H<sub>2</sub>O<sub>2</sub>, kept 2 hrs. at 40.degree. and 12 hrs. at 20.degree., evapd. in vacuo, the viscous residue heated 1 hr. at 40.degree. with excess 2N NaOH, the mixt. poured into hot 2N HCl and cooled, and the product isolated with EtOAc yielded VI, b<sub>0.2</sub> 129-30.degree.. VI (1.5 g.) in 7 cc. C<sub>5</sub>H<sub>5</sub>N treated at 0.degree. during 15 min. with 1.8 g. p-MeC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>Cl in small portions, refrigerated 2 hrs., poured into excess cold 2N HCl, extd. with C<sub>6</sub>H<sub>6</sub>, the ext. evapd. in vacuo, and

the residue fractionally crystd. from C<sub>6</sub>H<sub>6</sub> yielded cis-p-toluenesulfonate of VI, m. 102-3.degree., and 2.3 g. trans-p-toluenesulfonate of VI, m. 133-5.degree.. VI (5.8 g.) in 100 cc. glacial AcOH treated at 10.degree. with 2.5 g. CrO<sub>3</sub> in 60 cc. 80% AcOH, kept 7 days at room temp., concd. in vacuo to 25 cc., dild. with 200 cc. H<sub>2</sub>O, extd. 24 hrs. with Et<sub>2</sub>O, and the ext. **distd.** gave 4 g. 2-hydroxy-3-cyclohexanone-1-acetic acid **lactone** (VII), b<sub>0.5</sub> 147-50.degree., m. 50.degree.; semicarbazone, needles, m. 201-2.degree. (MeOH); oxime m. 119-20.degree. (Et<sub>2</sub>O). VII (10.7 g.) in 100 cc. dry C<sub>6</sub>H<sub>6</sub> treated with 5.1 g. (CH<sub>2</sub>OH)<sub>2</sub> and 0.2 g. PhSO<sub>3</sub>H, the mixt. refluxed about 3 hrs. with the **azeotropic** removal of 1.25 cc. H<sub>2</sub>O, and **distd.** yielded 3 g. ethylene ketal of cis-2-hydroxy-3-cyclohexanone-1-acetic acid **lactone** (VIII), b<sub>0.4</sub> 129-30.degree., and 9 g. trans-isomer (IX) of VIII, b<sub>0.4</sub> 135-6.degree., m. 60.degree. (MeOH). IX (5 g.) and 3.75 g. NaOH in 20 cc. H<sub>2</sub>O heated 0.5 hr. on the water bath, cooled, washed with Et<sub>2</sub>O, neutralized with 2N HCl with cooling, layered with Et<sub>2</sub>O, salted, and the Et<sub>2</sub>O layer worked up gave 4.5 g. ethylene ketal of trans-2-hydroxy-3-cyclohexanone-1-acetic acid, flakes, m. 111.degree.. IX (7 g.) and 5 g. NaOH in 25 cc. H<sub>2</sub>O heated 0.5 hr. on the water bath, treated with 15.7 g. MgSO<sub>4</sub>.7H<sub>2</sub>O in 10 cc. hot H<sub>2</sub>O, cooled after 10 min. to 5.degree., treated dropwise during 0.5 hr. with 1.95 cc. Br, stirred 2 hrs., layered with Et<sub>2</sub>O, acidified with 6M H<sub>2</sub>SO<sub>4</sub>, the Et<sub>2</sub>O layer worked up, and the residue digested with EtOAc and filtered off gave 5 g. monoethylene ketal (X) of 2,3-cyclohexanedione-1-acetic acid (XI), m. 129-30.degree. (EtOAc). X (5 g.) in 40 cc. Ac<sub>2</sub>O heated 1 hr. at 150.degree. with 1 g. NaOAc and evapd. in vacuo, the residue dissolved in EtOAc, and the soln. washed, dried, and **distd.** yielded 3 g. ethylene ketal (XII) of the enol **lactone** of XI, b<sub>0.17</sub> 125-30.degree.. XII (2 g.) in 40 cc. glacial AcOH hydrogenated over 1 g. Pd-BaSO<sub>4</sub> during 0.5 hr. and centrifuged, the supernatant evapd., the residue treated with MeOH, and filtered off yielded 0.4 g. IX, m. 60.degree.; the filtrate evapd. in vacuo and **distd.** yielded 1.2 g. VIII, b<sub>0.17</sub> 130-1.degree.. XII (0.5 g.) in abs. EtOH hydrogenated gave 0.35 g. IX, m. 60.degree.. XII (3 g.) and 10 cc. 0.1N HCl heated slowly to 110.degree., cooled, extd. with EtOAc, and the ext. worked up yielded 1 g. enollactone of XI, b<sub>0.5</sub> 145-8.degree.. 1,2-Cyclohexanedione (XIII) (17 g.) and 125 cc. Ac<sub>2</sub>O refluxed 3 hrs. and **distd.** yielded 15 g. 2-acetoxy-1-cyclohexen-3-one (XIV), b<sub>12</sub> 129-30.degree.; semicarbazone, needles, m. 174-5.degree. (MeOH). XIV (10 g.) in 100 cc. dry C<sub>6</sub>H<sub>6</sub> treated in the usual manner with 4 g. (CH<sub>2</sub>OH)<sub>2</sub> and 0.2 g. PhSO<sub>3</sub>H and fractionated yielded 8 g. ethylene ketal (XV) of XIV, b<sub>12</sub> 125-6.degree.. XIII (11 g.) in 100 cc. dry C<sub>6</sub>H<sub>6</sub> refluxed with the **azeotropic** removal of H<sub>2</sub>O with 6.4 g. (CH<sub>2</sub>OH)<sub>2</sub> and 0.2 g. PhSO<sub>3</sub>H and fractionated gave 3 g. monoethylene ketal (XVI) of

XIII, b12 107-11.degree. [semicarbazone m. 201-2.degree. (MeOH)], and XV, b12 114-25.degree.. XV (5 g.) refluxed 1 hr. with 2.5% alc. KOH and evapd. in vacuo, the residue neutralized with dil. HCl and extd. with Et2O, and the ext. worked up gave 3 g. XVI, b12 110-11.degree..

CC 10D (Organic Chemistry: Alicyclic Compounds)

IT **Lactones**

(hydroaromatic oxo-)

IT Cyclic compounds

(**lactones**, oxo-)

IT 2,7(3H,4H)-Benzofurandione, 5,6-dihydro-

2-Cyclohexen-1-one, 2-hydroxy-, semicarbazone

Cyclohexaneacetic acid, 2,3-dihydroxy-, cis-, .gamma.-

**lactones**

Cyclohexaneacetic acid, 2,3-dihydroxy-, p-toluenesulfonates

Cyclohexaneacetic acid, 2,3-dihydroxy-, trans-, .gamma.-

**lactones**

Cyclohexanemalonic acid, 2,3-dihydroxy-, Et ester

IT 100378-60-7, Cyclohexaneacetic acid, 2-hydroxy-3-oxo-, .gamma.-

**lactone**

(and derivs.)

IT 2138-99-0, 2-Cyclohexene-1-malonic acid 3675-31-8,

2-Cyclohexene-1-acetic acid 4746-91-2, 1,4-Dioxaspiro[4.5]

**decane**-7-acetic acid, 6-hydroxy-, .gamma.-**lactone**

4746-96-7, 1,4-Dioxaspiro[4.5]decan-6-one 5011-76-7,

2-Cyclohexen-1-one, 2-hydroxy-, acetate 6305-63-1,

2-Cyclohexene-1-malonic acid, diethyl ester 91492-30-7,

1,4-Dioxaspiro[4.5]decan-6-one, semicarbazone 94269-63-3,

1,4-Dioxaspiro[4.5]**decane**-7-acetic acid, 6-oxo-

98954-75-7, Cyclohexanemalonic acid, 2,3-dihydroxy-, .gamma.-

**lactone** 99173-45-2, 1,4-Dioxaspiro[4.5]dec-6-en-6-ol,

acetate 99186-77-3, 1,4-Dioxaspiro[4.5]dec-6-ene-7-acetic acid,

6-hydroxy-, .gamma.-**lactone** 99974-68-2,

1,4-Dioxaspiro[4.5]**decane**-7-acetic acid, 6-hydroxy-

105540-10-1, m-Menth-4-ene-1-carboxylic acid, methyl ester

105540-11-2, o-Menth-3-ene-1-carboxylic acid, methyl ester

108372-57-2, 1-Cyclohexene-1-acetic acid, 2-hydroxy-3-oxo-, .gamma.-

**lactone** 132465-78-2, m-Menth-5-ene-3-carboxylic acid,

ethyl ester 132465-79-3, o-Menth-5-ene-2-carboxylic acid, ethyl

ester

(prepn. of)

L35 ANSWER 10 OF 20 HCA COPYRIGHT 2005 ACS on STN

52:29753 Original Reference No. 52:5307h-i,5308a-i,5309a-g

Bicyclo[3.1.0]hexane derivatives. I. Synthesis of

bicyclo[3.1.0]-2-hexanone and methyl bicyclo[3.1.0]hexane-1-

carboxylate. Nelson, Norman A.; Mortimer, George A. (Massachusetts

Inst. of Technol., Cambridge). Journal of Organic Chemistry, 22,

1146-53 (Unavailable) 1957. CODEN: JOCEAH. ISSN: 0022-3263. OTHER SOURCES: CASREACT 52:29753.

AB Reaction of 4-tosyloxycyclohexanone (I) and 4-dimethylaminocyclohexanone methiodide (II) with strong bases formed bicyclo[3.1.0]hexan-2-one (III). This type of intramol. anionic displacement reaction was applied in the prepn. of methyl bicyclo[3.1.0]-hexane-1-carboxylate (IV) from Me cis-3-brosyloxycyclohexanecarboxylate (V). Similar base catalyzed reactions of Me 3,4-epoxycyclohexanecarboxylate (VI) resulted in transesterification reactions and intermol. attack of the epoxide ring rather than an intramol. displacement reaction. An attempted synthesis of sabina ketone was described. Hydroquinone (611 g.), 700 ml. 95% alc., and 6 teaspoonfuls Raney Ni shaken in H 4.5 hrs. at 140.degree., the catalyst removed from the hot soln., and the filtrate cooled gave 257 g. mixt. (VII) of 90% trans- and 10% cis-1,4-cyclohexanediols (VII), m. 131-41.5.degree.. VII (50 g.) in 400 ml anhyd. C<sub>5</sub>H<sub>5</sub>N stirred 1 hr. with 82 g. p-MeC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>Cl and refrigerated 18 hrs. gave 95.6 crude 4-tosyloxycyclohexanol (VIII). VIII (38.8 g.), 38 g. Me<sub>2</sub>CO, and 80 ml. AcOH treated dropwise during 13 min. at 10.degree. with 21 g. CrO<sub>3</sub> in 17 ml. H<sub>2</sub>O and 3.5 ml. AcOH, after 0.5 hr. the mixt. poured into Et<sub>2</sub>O, the Et<sub>2</sub>O washed with H<sub>2</sub>O, NaHCO<sub>3</sub> soln., H<sub>2</sub>O, dried, concd. and crystd. gave 20.7 g. I, m. 97.2-7.8.degree. (Et<sub>2</sub>O-hexane); 2,4-dinitrophenylhydrazone, m. 150.4-50.6.degree. (alc.-CHCl<sub>3</sub>),  $\lambda$ . 361 m. $\mu$ .,  $\epsilon$ . 23,500; semicarbazone, m. 140.3-40.7.degree. (decompn.) (alc.),  $\lambda$ . 227.5 m. $\mu$ .,  $\epsilon$ . 26,300. I (3.8 g.), 0.36 g. NaH, 50 ml. dioxane, and 1 drop abs. alc. refluxed 2.5 hrs. and the product **distd.** gave 0.87 g. III, b<sub>13</sub>, 58.degree., n<sub>25D</sub> 1.4706; 2,4-dinitrophenylhydrazone (VIIIa), m. 175.5-6.1.degree. (alc.-C<sub>6</sub>H<sub>6</sub>),  $\lambda$ . 369 m. $\mu$ .,  $\epsilon$ . 23,750. I (7.1 g.) and 100 ml. dioxane treated dropwise with 49.5 ml. 0.53N Ph<sub>3</sub>CNa in Et<sub>2</sub>O, the solvent **distd.** slowly during 2.3 hrs. to 99.degree., the mixt. cooled, 100 ml. each H<sub>2</sub>O and Et<sub>2</sub>O added, the Et<sub>2</sub>O layer concd., and **distd.** gave Ph<sub>3</sub>CH; the residue dissolved in Et<sub>2</sub>O, the Et<sub>2</sub>O removed, and the product **distd.** gave 1.44 g. III. I (4.6 g.) in 75 ml. tert-BuOH treated during 5 min. with 0.017 mole KOBu-tert in 25 ml. tert-BuOH, the mixt. refluxed 2.5 hrs., and the product **distd.** through a 40 cm. Vigreux column gave 87% III, identified as its 2,4-dinitrophenylhydrazone. Thus, III **azeotropes** with tert-BuOH and could not be obtained by fractional **distn.** 4-Isopropylanisole (20 g.) (b<sub>21</sub> 95-6.5.degree., n<sub>25D</sub> 1.5004) and 50 ml. Et<sub>2</sub>O treated with 500 ml. anhyd. NH<sub>3</sub> and during 5 min. with 5.1 g. Li wire, after 10 min. 55 ml. abs. alc. added dropwise during 3 min., then 2.7 g. further Li wire and 30 ml. alc. added, and the product isolated in the usual way gave 17.5 g. 2,5-dihydro-4-isopropylanisole (IX), b<sub>21</sub> 98-9.degree., n<sub>25D</sub> 1.4748; ultraviolet spectrum of the **distillate** at 277 and 284 m. $\mu$ . indicated no starting

material. IX gave 91% 4-isopropylcyclohex-3-enone 2,4-dinitrophenylhydrazone (X), 114.2-17.degree., .lambda. 364 m.mu., .epsilon. 23,150. IX (10 g.), 1.0 g. (CO<sub>2</sub>H)<sub>2</sub>, 40 ml. H<sub>2</sub>O, 90 ml. Me<sub>2</sub>CO, and 50 ml. MeOH stirred 75 min. at room temp. gave after **distn.** 8.2 g. 4-isopropylcyclohex-3-enone (XI), b<sub>9</sub> 73-5.degree., .lambda. 5.83 .mu. showing the absence of 4-isopropylcyclohex-2-enone (XIa). IX (36.7 g.), 38.1 g. (CH<sub>2</sub>OH)<sub>2</sub>, 300 ml. C<sub>6</sub>H<sub>6</sub>, and 0.5 g. p-MeC<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>H refluxed 2.5 hrs. with **distn.** of 75 ml. liquid, the soln. extd. with aq. Na<sub>2</sub>CO<sub>3</sub>, the aq. layer extd. with Et<sub>2</sub>O, the combined org. layers concd., and the residue fractionally **distd.** gave 31.1 g. XI ethylene ketal (XII), b<sub>20</sub> 114.5-18.degree., n<sub>25D</sub> 1.4733. XII was converted at 0.degree. to X in 70% yield. XII (10.0 g.) and 50 ml. Et<sub>2</sub>O treated 45 min. at 0.degree. with passage of HCl, then left overnight, and the residue fractionally **distd.** gave 9.4 g. 4-chloro-4-isopropylcyclohexanone ethylene ketal (XIII), b<sub>0.73</sub> 90.0-0.5.degree., n<sub>25D</sub> 1.4813. XIII did not form a dinitrophenylhydrazone at 0.degree., but XIa 2,4-dinitrophenylhydrazone was formed at 45.degree. and above, m. 132-2.4.degree., .lambda. 379 m.mu., .epsilon. 27,300. The attempted Markovnikov addn. of HCl to XI at 10.degree. gave a product which by infrared analysis was shown to be a mixt. of XI and XIa. XIII treated by direct hydrolysis in aq. Me<sub>2</sub>CO with p-MeC<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>H, aq. alc. HCl, and cold concd. HCl (acid catalyzed transketalizations using Me<sub>2</sub>CO and AcCO<sub>2</sub>H as acceptors were also investigated) gave either starting material or a mixt. of unsatd. ketones. 4-Chloro-4-isopropylcyclohexanone was not obtained in any case. p-H<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>OH (500 g.) in 600 ml. H<sub>2</sub>O and 100 ml. AcOH was acetylated at 60.degree., the mixt. heated an addnl. hr., left overnight, and 524 g. p-AcNHC<sub>6</sub>H<sub>4</sub>OH (XIV) isolated, m. 168-70.degree.. XIV (322 g.) in alc. hydrogenated over Raney Ni at 180.degree. and 2000 lb./sq. in. gave 334 g. 4-acetamidocyclohexanol (XV) as an isomeric mixt. XV (50 g.), 100 ml. H<sub>2</sub>O, and 29.5 g. KOH refluxed 18.5 hrs., the soln. concd. and extd. with tetrahydrofuran, and the residue carefully warmed with 43 ml. 98-100% HCO<sub>2</sub>H and 49 ml. 37% HCHO, then refluxed 23 hrs., 27 ml. concd. HCl added, the mixt. concd. in vacuo to a sirup, then made alk. with 50% NaOH, extd. with tetrahydrofuran, and **distd.** gave 18.9 g. 4,4-dimethylcyclohexanol (XVI), b<sub>14</sub> 121-3.degree., identical with another specimen prepd. in 19% yield from p-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>OH. XVI (40 g.), 165 ml. ice and H<sub>2</sub>O, and 43 ml. concd. HCl treated at 20.degree. with 32.2 g. K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, after 0.5 hr. the mixt. cooled 2 days, the solids removed, the filtrate poured into 300 g. KOH and 300 ml. H<sub>2</sub>O, extd. with Et<sub>2</sub>O, and the product **distd.** gave 7.3 g. unchanged XVI and 12.2 g. 4-dimethylaminocyclohexanone (XVII), b<sub>12</sub> 95.degree., n<sub>25D</sub> 1.4706; 2,4-dinitrophenylhydrazone, m. 117.5-18.degree. (MeOH); p-toluenesulfonic acid salt, m. 114.2-15.6.degree. (EtOAc). XVII (3.4 g.), 7 g. MeI, and 25 ml.



Et<sub>2</sub>O refrigerated overnight gave 97% II, m. 274.degree. (alc.). II (3.9 g.) and 100 ml. tert-BuOH treated 5 min. with 0.0135 mole KOBu-tert in 25 ml. tert-BuOH, mixt. refluxed 2.5 hrs., H<sub>2</sub>O, K<sub>2</sub>CO<sub>3</sub>, and Et<sub>2</sub>O added, and the org. layer dried and **distd.** gave on treatment with 2,4-dinitrophenylhydrazine 42% crude VIIIA. m-HOC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>Me in MeOH hydrogenated over Raney Ni at 180.degree. and 1800 lb./sq. in. gave 71% crude Me cis-3-hydroxycyclohexanecarboxylate (XVIII), b<sub>1-2</sub> 103-10.degree., contg. a small amt. of the corresponding cyclic **lactone** as an impurity. XVIII on sapon. gave the known cis-3-hydroxycyclohexanecarboxylic acid, m. 121.5-5.5.degree.. XVIII (15.4 g.), 100 ml. anhyd. C<sub>5</sub>H<sub>5</sub>N, and 25 g. p-BrC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>Cl stirred 1 hr., left in the refrigerator overnight, the filtrate shaken with dil. Na<sub>2</sub>CO<sub>3</sub>, and extd. with Et<sub>2</sub>O gave 25.5 g. V, m. 89.5-90.degree. (C<sub>6</sub>H<sub>6</sub>-C<sub>5</sub>H<sub>12</sub>). V (38.1 g.) and 300 ml. tert-BuOH refluxed 25 min. with 0.101 mole KOBu-tert in 100 ml. tert-BuOH, the product extd., and **distd.** gave 11.72 g. IV, b<sub>22</sub> 79.degree., n<sub>25D</sub> 1.4615. IV did not decolorize a 2% KMnO<sub>4</sub> soln. in 2 min.,  $\lambda$  3.24 and 3.32  $\mu$ . attributed to the C-H stretching of the methylene H on a cyclopropane ring and a strong band at 9.65  $\mu$ . attributed to the cyclopropane symmetric vibration. The vapor phase chromatogram showed a single sharp band, indicating the absence of olefinic isomers. IV (0.56 g.) and 10 ml. satd. MeOH-NH<sub>3</sub> heated 4 days at 100.degree. in a sealed tube gave 0.33 g. bicyclo[3.1.0]-hexane-1-carboxamide, m. 161-2.degree. (cyclohexane-C<sub>6</sub>H<sub>6</sub>), 3.32  $\mu$ . as well as a strong band at 9.94  $\mu$ . characteristic of the 3-membered ring. Butadiene and CH<sub>2</sub>:CHCO<sub>2</sub>Me gave 91% Me 3-cyclohexenecarboxylate (XIX), b<sub>20</sub> 80.degree., n<sub>25D</sub> 1.4589. XIX (0.69 g.) and 10 ml. satd. MeOH-NH<sub>3</sub> heated 2 days at 100.degree. in a sealed tube gave 0.48 g. 3-cyclohexenecarboxamide, m. 155.5-6.5.degree. (cyclohexane-C<sub>6</sub>H<sub>6</sub>). Com. HCO<sub>3</sub>H (0.10 mole) in 30 ml. CH<sub>2</sub>Cl<sub>2</sub> shaken with 4 g. NaOAc.3H<sub>2</sub>O, added dropwise during 10 min. to a cold soln. of 7.0 g. XIX in 28 ml. CH<sub>2</sub>Cl<sub>2</sub>, the mixt. left 2 days at room temp., a 40% NaOH soln. added, and the product extd. with CH<sub>2</sub>Cl<sub>2</sub> gave 2.8 g. unchanged XIX and 3.6 g. VI, b<sub>22</sub> 115-17.degree., n<sub>25D</sub> 1.4625. Large scale preps. gave comparable yields. VI (7.41 g.) and 50 ml. tert-BuOH stirred 5 min. with 0.047 mole KOBu-tert in 50 ml. tert-BuOH and refluxed 1 hr. gave 6.63 g. tert-Bu 3,4-epoxycyclohexanecarboxylate (XX), b<sub>1.4</sub> 80.5-1.5.degree., n<sub>25D</sub> 1.4525, bands at 7.22 and 7.33  $\mu$ . characteristic of the tert-Bu group. LiAlH<sub>4</sub> reduction of XX gave a product as a viscous oil whose infrared spectrum showed the absence of the tert-Bu group. Thus, this group in XX must have been present as an ester and not an ether. Similarly, 7.91 g. VI in 100 ml. tert-BuOH refluxed 8.5 hrs. with 0.052 mole KOBu-tert in tert-BuOH and the product fractionally **distd.** gave 4.38 g. XX and 2.54 g. tert-Bu 3,4-methoxyhydroxycyclohexanecarboxylate, b<sub>0.03</sub> 74.degree., n<sub>25D</sub> 1.4575,  $\lambda$  2.88  $\mu$ . for associated and 2.78  $\mu$ . for unassociated OH and 7.22 and 7.34  $\mu$ . for the tert-Bu

group.

CC 10 (Organic Chemistry)  
 IT 103-90-2, Acetanilide, 4'-hydroxy- 932-01-4, Cyclohexanol,  
 4,4-dimethyl- 2158-60-3, 1,4-Dioxaspiro[4.5]dec-7-ene,  
 8-isopropyl- 2158-60-3, 3-Cyclohexen-1-one, 4-isopropyl-, cyclic  
 ethylene acetal 4160-49-0, Bicyclo[3.1.0]hexan-2-one 4771-81-7,  
 3-Cyclohexene-1-carboxamide 5259-66-5, 3-Cyclohexen-1-one,  
 4-isopropyl- 6493-77-2, 3-Cyclohexene-1-carboxylic acid, methyl  
 ester 19203-59-9, Bicyclo[3.1.0]hexan-2-one, (2,4-  
 dinitrophenyl)hydrazone 22267-35-2, Cyclohexanecarboxylic acid,  
 3-hydroxy-, cis- 23363-88-4, Acetamide, N-4-hydroxycyclohexyl-  
 25090-51-1, Bicyclo[3.1.0]hexane-1-carboxylic acid, methyl ester  
 37722-82-0, Cyclohexanecarboxylic acid, 3-hydroxy-, methyl ester  
 40731-98-4, 1-Indanone, 4-hydroxy- 92121-36-3,  
 1,4-Cyclohexanediol, trans-, p-toluenesulfonate 98431-50-6,  
 Bicyclo[3.1.0]hexane-1-carboxamide 98954-37-1,  
 1,4(3aH)-Indandione, tetrahydro- 99180-72-0, Ether,  
 4-isopropyl-1,4-cyclohexadien-1-ylmethyl 105339-67-1,  
 Cyclohexanecarboxylic acid, 4-hydroxy-3-methoxy-, tert-butyl ester  
 105583-23-1, Cyclohexanone, 4-chloro-4-isopropyl-, cyclic ethylene  
 acetal 105583-23-1, 1,4-Dioxaspiro[4.5]decane,  
 8-chloro-8-isopropyl- 108236-09-5, 3-Cyclohexen-1-one,  
 4-isopropyl-, (2,4-dinitrophenyl)hydrazone 120088-30-4, Ammonium,  
 trimethyl(4-oxocyclohexyl)-, iodide 132961-64-9,  
 1,4-Cyclohexanediol, cis-, p-toluenesulfonate  
 (prepn. of)

L35 ANSWER 11 OF 20 HCA COPYRIGHT 2005 ACS on STN

51:90660 Original Reference No. 51:16434e-i,16435a New synthesis of  
 6-thioctic acid (DL-.alpha.-lipoic acid). Segre, Augusto; Viterbo,  
 Rene; Parisi, Giovanni (Farmochimica Sutolo-Calosi S.F.A., Naples,  
 Italy). Journal of the American Chemical Society, 79, 3503-5  
 (Unavailable) 1957. CODEN: JACSAT. ISSN: 0002-7863. OTHER  
 SOURCES: CASREACT 51:90660.

AB Cyclohexanone (29 g.), 85 g. pyrrolidine, and 200 cc. dry C6H6  
 refluxed 1.5 hrs. with the **azeotropic** removal of 6 cc. H2O  
 and evapd. in vacuo, the residual oily enamine treated in 150 cc.  
 dry refluxing C6H6 with 37.5 g. BrCH2CO2Et, the mixt. refluxed 1  
 hr., the excess bromo ester removed in vacuo, the thick residue  
 refluxed 2 hrs. with 100 cc. MeOH and 20 cc. H2O; the soln. concd.  
 in vacuo, the residue dild. with H2O and extd. with Et2O, and the  
 ext. worked up yielded 38.6 g. Et cyclohexanone-2-acetate (I), b13  
 131-4.degree., nD23 1.4564; 2,4-dinitrophenylhydrazone (II), m.  
 126.degree.. I (38.5 g.), 14.5 g. (CH2OH)2, and 50 mg. p-MeC6H4SO3H  
 in 100 cc. dry PhMe refluxed 3 hrs. with the removal of 4.5 cc. H2O,  
 cooled, washed, dried, and **distd.** gave 42 g. ethylene  
 ketal (III) of I, b13 145-7.degree., nD23 1.4630. III treated with  
 2,4-(O2N)2C6H3NHNH2 (IV) gave II. III (32 g.) in dry Et2O reduced

with 4 g.  $\text{LiAlH}_4$  in 350 cc. dry  $\text{Et}_2\text{O}$  yielded 25 g. 2-hydroxyethylcyclohexanone ethylene ketal (V),  $b_{13}$  148-50.degree.,  $n_{\text{D}23}$  1.4822. V treated with IV yielded the 2,4-dinitrophenylhydrazone of 2-hydroxycyclohexanone, m. 145-6.5.degree.. III (5 g.) in 25 cc. boiling abs.  $\text{EtOH}$  treated with stirring during 0.5 hr. with 30 cc. abs.  $\text{EtOH}$ , cooled, evapd. to near dryness, poured into  $\text{H}_2\text{O}$ , and extd. with  $\text{Et}_2\text{O}$ , and the ext. worked up gave 3.7 g. V,  $b_{13}$  148-50.degree.. V (2 g.) in 6 cc. pyridine treated 2 hrs. at room temp. with 2 cc.  $\text{Ac}_2\text{O}$ , poured into ice  $\text{H}_2\text{O}$ , and extd. with  $\text{Et}_2\text{O}$ , and the extd. worked up yielded 2.1 g. ethylene ketal (VI) of 2-acetoxyethylcyclohexanone (VII),  $b_{13}$  152.degree.,  $n_{\text{D}27}$  1.4632; VI gave the 2,4-dinitrophenylhydrazone (VIII) of VII, m. 109-11.degree.. VI (2 g.) and 75 mg.  $p\text{-MeC}_6\text{H}_4\text{SO}_3\text{H}$  in 20 cc.  $\text{Me}_2\text{CO}$  refluxed 1 hr. and evapd. in vacuo below 40.degree., the oily residue dissolved in  $\text{Et}_2\text{O}$ , and the soln. washed, dried, and **distd.** gave 1.55 g. VII,  $b_{15}$  142-6.degree.,  $n_{\text{D}27}$  1.4565; it gave VIII. VII (4.7 g.) in 16.3 cc.  $\text{Ac}_2\text{O}$  (contg. 28.0 mg. active  $\text{O}/\text{cc.}$ ) dild. with  $\text{CHCl}_3$ , washed, dried, and **distd.** yielded 3.3 g. 6-hydroxy-8-acetoxyoctanoic acid **lactone** (IX),  $b_{0.5}$  126-30.degree.,  $n_{\text{D}23}$  1.4595. IX (2.2 g.), 6.5 g.  $\text{SC}(\text{NH}_2)_2$ , and 8.66 g. 57%  $\text{HI}$  refluxed 36 hrs., treated with 35 cc. 30% aq.  $\text{KOH}$ , refluxed 12 hrs. in the dark under  $\text{N}$ , washed with  $\text{Et}_2\text{O}$ , acidified with 2N  $\text{HCl}$ , and extd. with  $\text{CHCl}_3$ , and the ext. worked up gave 1.84 g. 6,8-dithiolooctanoic acid (X),  $b_{1.5}$  180.degree.,  $n_{\text{D}22}$  1.5225. X (1.01 g.) in 2.3 cc. 2N  $\text{NaOH}$  dild. with 17 cc.  $\text{H}_2\text{O}$  contg. 3.5 mg.  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , the soln. treated 10 hrs. with a slow stream of  $\text{O}$ , washed with  $\text{CHCl}_3$ , acidified with 2N  $\text{HCl}$ , and extd. with  $\text{CHCl}_3$ , the ext. evapd. to dryness, and the residual yellow oil triturated with petr. ether (b. 40-60.degree.) and recrystd. from petr. ether yielded 0.8 g. pure 6-thioctic acid, m. 61-2.degree.; S-benzylisothiuronium salt, m. 153-4.degree. (from abs.  $\text{MeOH}$ ) (m. p. 132-4.degree. was observed once).

CC 10 (Organic Chemistry)

IT 57133-56-9, 1,4-Dioxaspiro[4.5]**decane**-6-ethanol  
(and derivs.)

IT 462-20-4, Octanoic acid, 6,8-dimercapto- 57133-55-8,  
1,4-Dioxaspiro[4.5]**decane**-6-acetic acid, ethyl ester  
92016-30-3, Octanoic acid, 6,8-dihydroxy-, .epsilon.-**lactone**  
, acetate  
(prepn. of)

L35 ANSWER 12 OF 20 HCA COPYRIGHT 2005 ACS on STN

51:66447 Original Reference No. 51:12012f-i,12013a-g The steric course of the diene synthesis from 1,3-cycloheptadiene with maleic anhydride. A study of bridged bicyclic ring systems. Alder, Kurt; Molls, Hans Heinz (Univ. Cologne, Germany). *Chemische Berichte*, 89, 1960-71 (Unavailable) 1956. CODEN: CHBEAM. ISSN: 0009-2940.

AB It is established that the adduct (I) from 1,3-cycloheptadiene (II)

and maleic anhydride is 1,4-endopropylene-5-cyclohexene-2,3-dicarboxylic anhydride and has the endo cis configuration. II, b150 71.5.degree.,  $\lambda$ . 247  $\mu$ . (log  $\epsilon$ . 3.944), was prepd. from cyclohexanone and CH<sub>2</sub>N<sub>2</sub> via cycloheptanone, b80 105.degree.; II with maleic anhydride in boiling o-xylene gave 90% I, m. 114.degree. (from EtOAc). II reacted much more slowly than cyclohexadiene. Similarly an adduct (III), b0.02 79-83.degree., was prepd. from II with fumaryl chloride. III with 10 parts H<sub>2</sub>O contg. HCl heated slightly and then cooled, gave the trans-dicarboxylic acid (IV), m. 202-3.degree. (from HOAc-H<sub>2</sub>O), which was hydrogenated with Pt to give the known transdihydro acid, m. 228-9.degree.; the latter did not yield a trans anhydride by heating to 100.degree. with Ac<sub>2</sub>O. The proof of configuration was continued by degradation to the following cycloheptanetetracarboxylic acids and derivs.: the all-cis-1,2,3,4-acid (V), its 2,3-monoanhydride (VI), the 1,2,3,4-dianhydride (VII), the 1-cis-2-cis,3-trans-4-trans-dianhydride (VIII), the 1-cis-2-cis, 3-trans-4-cis-acid (IX), and the 1-cis-2-cis,3-trans-4-cis-dianhydride (X). Gradual addn. of 10 g. I to 160 cc. boiling HNO<sub>3</sub> (d. 1.4), 2 hrs. reflux on an oil bath at 170.degree., 5 cycles of vacuum evapn. and soln. in 20 cc. H<sub>2</sub>O, followed by trituration with EtOAc and crystn. from 75% HCO<sub>2</sub>H gave 25% VI, decomp. 216.degree., stable towards dehydrating agents; the di-Me ester m. 163.degree. (prepd. with CH<sub>2</sub>N<sub>2</sub> in Et<sub>2</sub>O). Ozonization of I in glacial HOAc followed by treatment with H<sub>2</sub>O<sub>2</sub> gave 28% VI. NaMnO<sub>4</sub> (15% aq.) added until red to a clear soln. of 5 g. I in 200 cc. aq. Na<sub>2</sub>CO<sub>3</sub> at 50.degree. and while passing CO<sub>2</sub>, the mixt. decolorized with a few drops of MeOH, filtered, washed, concd. in vacuo to 50 cc., acidified to Congo red, sepd. from 0.7 g. ppt. of I, evapd. to dryness, and extd. 10 hrs. with EtOAc yielded 43% 5,6-dioxo-1,4-endopropylencyclohexane-2,3-dicarboxylic acid (XI), m. 193.degree. (from MeCN-ligroine); di-Me ester, m. 152.degree. (from C<sub>6</sub>H<sub>6</sub>); quinoxaline deriv. of the ester, m. 190.degree. (from MeOH). Oxidation of XI with 15 parts 1:3 H<sub>2</sub>O<sub>2</sub>-HOAc preheated to 85.degree. and then heated 1 hr. to 100.degree. yielded 72% VI. V, decomp. 180.degree., was obtained in 70% yield from VI by refluxing 30 hrs. with 30 parts H<sub>2</sub>O contg. a trace of HCl, evapg. in vacuo to 1 cc. and adding 5 cc. concd. HCl, or in 60% yield by 2 hrs. boiling with a slight excess of Na<sub>2</sub>CO<sub>3</sub>, acidifying with dil. HCl, and extg. several days with EtOAc. VII, m. 230.degree., was obtained from V with 20 parts AcCl after 3 weeks at room temp. or 6 hrs. heating on the H<sub>2</sub>O bath and **distg.** in vacuo. Repeated crystn. of VII in Ac<sub>2</sub>O or MeCN caused a drop of m.p. and then a rise to a const. 223-4.degree., denoting isomerization to VIII, which was also obtained directly from V by refluxing 1 hr. with 20 parts Ac<sub>2</sub>O. IX, m. 173.degree., was obtained from IV by oxidation with HNO<sub>3</sub> (35% yield) or O<sub>3</sub> (25%), and converted to X, decomp. 245-8.degree., by the procedures yielding VI from V; X isomerized to VIII, which was also prepd. directly from IX. A soln. of 2 g. I in dil. Na<sub>2</sub>CO<sub>3</sub>

treated with Br to persisting color, acidified, and concd. yielded the dicarboxylic acid bromohydrin (XII), m. 173.degree.; attempted lactonization with Ac<sub>2</sub>O yielded only the corresponding aceto bromo anhydride, m. 135.degree. (EtOAc), presumably because of the unfavorable OH position. A **lactone** deriv. (XIII), decomp. 193.degree., of XII was however obtained on the site of Br after 2 hrs. hydrolysis of 5 g. in 20 g. cc. 10% KOH on the H<sub>2</sub>O bath and extn. with EtOAc preceded and followed by evapn. The hydroxy **lactone** mono-Me ester, m. 148.degree. (EtOAc), was readily prepd. with CH<sub>2</sub>N<sub>2</sub>. Treatment of 2 g. I with 10 g. preheated H<sub>2</sub>O<sub>2</sub>-HOAc after 3 hrs. heating and thorough vacuum evapn. gave 95% very stable 5,6-epoxy-2,3-anhydride, m. 162.degree., converted to the diacetoxo anhydride (XIV), m. 170.degree., by 16 hrs. reflux of 3 g. with 20 cc. Ac<sub>2</sub>O and 0.5 cc. concd. HCl. From 3 g. XIV suspended in 10 cc. 2% HCl plus enough dioxane for soln., boiled 30 hrs., and concd. to 1 cc. was obtained 1.8 g. hydroxy **lactone**, m. 221.degree. (from MeOH), stereoisomeric with XIII, and the Me ester, m. 118.degree.. endo-cis-2,3-Dicarbomethoxy-1,4-endopropylencyclohexane, b<sub>12</sub> 177-8.degree., was prepd. from I by hydrogenation and 4 hrs. esterification of 40 g. with MeOH-H<sub>2</sub>SO<sub>4</sub>; the resulting 34 g. was dissolved in 100 cc. Et<sub>2</sub>O and reduced with LiAlH<sub>4</sub> to 97% 2,3-diol, m. 67.degree.. Treatment of the diol with Ac<sub>2</sub>O gave 90% diacetate, b<sub>0.03</sub> 125-6.degree., m. 37-8.degree., which was pyrolyzed to 20% 2,3-dimethylene compd. (XV), b<sub>30</sub> 102.9.degree., .lambda. 248 m.mu., by passing 20 drops/min. through glass wool into a vertical quartz tube heated to 520.degree. in the presence of N, collecting the product by cooling, **distg.** as the HOAc **azeotrope**, and sepg. with H<sub>2</sub>O and Et<sub>2</sub>O. XV in C<sub>6</sub>H<sub>6</sub> with maleic anhydride formed an adduct, m. 155.degree. (from EtOAc); similarly XV with fumaryl chloride formed an adduct, hydrolyzed in dil. Na<sub>2</sub>CO<sub>3</sub> to the trans-dicarboxylic acid, m. 214.degree. (from EtOAc-ligroine). 1,4-Endoethylene analogs were prepd. by similar methods: the unsatd. 2,3-diol, m. 89.degree. (diacetate, b<sub>12</sub> 176.degree.); the hydrogenated diacetate, b<sub>12</sub> 179.degree.; the hydrocarbon, b<sub>50</sub> 93.degree., n<sub>D20</sub> 1.5106, d<sub>20</sub> 0.9184, .lambda. 249 m.mu.. The steric course of the diene synthesis of I from II follows the pattern of the 2 lower homologous dienes.

CC 10 (Organic Chemistry)

IT 502-42-1, Cycloheptanone 5684-39-9, 3-Oxatricyclo[3.3.2.0<sup>2,4</sup>] **decane**-9,10-dicarboxylic anhydride 36439-79-9, Bicyclo[2.2.2]octane, 2,3-dimethylene- 36439-81-3, Bicyclo[3.2.2]nonane, 6,7-dimethylene- 56306-07-1, 1,4-Ethanonaphthalene-6,7-dicarboxylic acid, 1,2,3,4,5,8-hexahydro-, dimethyl ester 100713-35-7, Bicyclo[3.2.2]nonane-6,7-dicarboxylic anhydride, 8-bromo-9-hydroxy-, acetate 100864-31-1, Bicyclo[2.2.2]oct-5-ene-2,3-dimethanol, diacetate 100883-85-0, 1,4-Ethanonaphthalene-6,7-dicarboxylic anhydride, 1,2,3,4,5,6,7,8-octahydro- 100957-09-3, 5,9-Ethano-1H-

benzocycloheptene-2,3-dicarbonyl chloride, 2,3,4,5,6,7,8,9-octahydro-  
 100964-45-2, Bicyclo[2.2.2]octane-2,3-dimethanol, diacetate  
 101088-98-6, 5,9-Ethano-1H-benzocycloheptene-2,3-dicarboxylic  
 anhydride, 2,3,4,5,6,7,8,9-octahydro- 101103-62-2,  
 Bicyclo[3.2.2]nonane-6,7-dicarboxylic anhydride, 8,9-dihydroxy-,  
 diacetate 101262-66-2, Bicyclo[3.2.2]nonane-2,3-dimethanol,  
 diacetate 105912-66-1, Bicyclo[3.2.2]nonane-6,7-dicarboxylic acid,  
 dimethyl ester 110440-44-3, 6,10-Ethano-6H-  
 cyclohepta[b]quinoxaline-12,13-dicarboxylic acid,  
 7,8,9,10-tetrahydro-, dimethyl ester  
 (prepn. of)

L35 ANSWER 13 OF 20 HCA COPYRIGHT 2005 ACS on STN

51:29700 Original Reference No. 51:5700i,5701a-i,5702a-d Structure of  
 the antibiotic methymycin. Djerassi, Carl; Zderic, John A. (Wayne  
 State Univ., Detroit, MI). Journal of the American Chemical  
 Society, 78, 6390-5 (Unavailable) 1956. CODEN: JACSAT. ISSN:  
 0002-7863.

GI For diagram(s), see printed CA Issue.

AB cf. C.A. 50, 14782f. Methymycin (I) is shown to have the structure  
 $\text{O.CHEt.CMe(OH).CH:CH.CO.CHMe.CH}_2\text{.CHMe.CH(OR).CHMe.CO}$  (II) [R =  
 2-(3-hydroxy-4-dimethylamino-6-methyltetrahydropyranyl)]. I (12.0  
 g.) refluxed 4 min. with 600 cc. 5N H<sub>2</sub>SO<sub>4</sub>, immediately cooled, dild.  
 with H<sub>2</sub>O, extd. with CHCl<sub>3</sub>, the ext. worked up, and the viscous oily  
 residue (6.45 g.) triturated with hexane yielded 1.91 g.  
 methynolide, II (R = H) (III), nearly colorless crystals, m.  
 163-5.degree. (from Et<sub>2</sub>O), [ $\alpha$ ]D 79.degree. (CHCl<sub>3</sub>), 63.degree.  
 (MeOH). III (310 mg.) heated overnight with 300 mg. LiAlH<sub>4</sub> in 50  
 cc. tetrahydrofuran, treated dropwise with satd. aq. Na<sub>2</sub>SO<sub>4</sub>,  
 filtered, the solvent removed, the residual oil dried  
**azeotropically** with C<sub>6</sub>H<sub>6</sub>, dissolved in EtOH, treated 44 hrs.  
 with 25 cc. 0.21N HIO<sub>4</sub>, dild. with H<sub>2</sub>O, **distd.** into 400  
 mg. 2,4-(O<sub>2</sub>N)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NHNH<sub>2</sub> in 50 cc. EtOH, and the product  
 chromatographed on 60 g. Al<sub>2</sub>O<sub>3</sub> yielded 140 g. 2,4-(O<sub>2</sub>N)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NHN:CH<sub>2</sub>Et  
 (IV). III (105 mg.) treated at 0.degree. overnight with Ac<sub>2</sub>O  
 pyridine gave 102 mg. acetate of III, m. 198-200.degree., with a  
 change of crystal form above 180.degree. from needles to irregular  
 plates (from Et<sub>2</sub>O), [ $\alpha$ ]D 93.degree. (CHCl<sub>3</sub>). III (400 mg.) in  
 10 cc. cold Me<sub>2</sub>CO treated dropwise with 0.3 cc. soln. of 2.67 g.  
 CrO<sub>3</sub> in 2.3 cc. concd. H<sub>2</sub>SO<sub>4</sub> dild. to 10 cc. with H<sub>2</sub>O, the soln.  
 dild. after 5 min. with 100 cc. H<sub>2</sub>O, extd. with CHCl<sub>3</sub>, the ext.  
 worked up, and the cryst. residue (360 mg.) chromatographed on Al<sub>2</sub>O<sub>3</sub>  
 yielded 300 mg. dehydromethynolide II [CH(OR) = CO] (V), m.  
 173-9.degree. (from Et<sub>2</sub>O hexane), [ $\alpha$ ]D 177.degree. (CHCl<sub>3</sub>). V  
 (50 mg.) refluxed 1 hr. with excess 0.2N alkali, acidified, the CO<sub>2</sub>  
 swept with N into standard base, and the soln. back-titrated gave  
 58% CO<sub>2</sub>. KMnO<sub>4</sub> (7.5 g.) in 150 cc. H<sub>2</sub>O added dropwise during 1.5  
 hrs. to 2.0 g. III in 50 cc. Me<sub>2</sub>CO, the mixt. stirred at room temp.

overnight, the soln. treated with 10 g. Na<sub>2</sub>SO<sub>3</sub>, 7.5 cc. concd. H<sub>2</sub>SO<sub>4</sub>, and a large amt. of NaCl, extd. with Et<sub>2</sub>O, the ext. evapd., and the residual yellow viscous oil (415 mg.) chromatographed on 10 g. Al<sub>2</sub>O<sub>3</sub> gave 80 mg. AcEtCHOCOCHMeCH.CHMe.CH<sub>2</sub>.CHMe.CO.O (VI), m. 55-6.degree. (from hexane). VI (60 mg.) refluxed 0.5 hr. with 6.5 cc. 5% aq. NaOH, slowly steam **distd.** into 10 cc. MeOH contg. 80 mg. 2,4-(O<sub>2</sub>N)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NHNH<sub>2</sub> and a few drops of concd. H<sub>2</sub>SO<sub>4</sub>, and the soln. allowed to stand overnight, refluxed 5 hrs., and cooled gave 18 mg. bis(2,4-dinitrophenylhydrazone) of AcCOEt, deep red crystals; the alk. steam **distn.** residue acidified strongly with H<sub>2</sub>SO<sub>4</sub>, salted, extd. with Et<sub>2</sub>O, the ext. evapd., and the amber, oily residue (46 mg.) chromatographed on 4 g. silica gel gave 21 mg. straw colored crystals which, sublimed at 110.degree./0.005 mm., gave 15 mg. O.CH(CHMeCO<sub>2</sub>H).CHMe.CH<sub>2</sub>.CHMe.CO. (VII), m. 124-7.degree. (from Et<sub>2</sub>O-hexane); the alk. exts. from the original KMnO<sub>4</sub> oxidation mixt. acidified, heavily salted, extd. with Et<sub>2</sub>O, and the product isolated with Et<sub>2</sub>O yielded 110 mg. O.CH[CHMeCO<sub>2</sub>CHEtCMe(OH)CO<sub>2</sub>H].CHMe.CH<sub>2</sub>.CHMe.CO (VIII), m. 164-72.degree., [.alpha.]D 52.degree. (Me<sub>2</sub>CO). VIII (50 mg.) treated 20 hrs. at room temp. with 73 mg. Pb(OAc)<sub>4</sub> and 4 cc. glacial AcOH and the product isolated with Et<sub>2</sub>O gave 8 mg. VI, m. 52-4.degree.. VIII sapond. with alkali yielded about 15% VII. The mother liquors from the isolation of VIII combined and chromatographed on 30 g. silica gel yielded 110 mg. oily crystals which, recrystd. several times, gave 20 mg. VII, m. 125-7.degree.. The mixt. from a similar KMnO<sub>4</sub> oxidation of III initially basified (instead of acidified) and then processed yielded 80 mg. VII, m. 126-8.degree., [.alpha.]D 38.degree.. VII treated 5 min. with CH<sub>2</sub>N<sub>2</sub> in Et<sub>2</sub>O gave the Me ester, m. 79-81 .degree. (from pentane). I (20 g.) and 60 cc. concd. H<sub>2</sub>SO<sub>4</sub> in 1 l. MeOH refluxed 5 hrs., kept at room temp. overnight, dild. with H<sub>2</sub>O, extd. with Et<sub>2</sub>O, the ext. evapd., the residual natural oil (6.91 g.) chromatographed on 210 g. deactivated Al<sub>2</sub>O<sub>3</sub>, and the resulting viscous oil (5.6 g.) rechromatographed 3 times on Al<sub>2</sub>O<sub>3</sub> yielded 2.25 g. O. CHEt.CMe.CHX.CH<sub>2</sub>.C.CHMe.CH<sub>2</sub>.CHMe.CH.CHMe.CO (IX) (X = MeO), m. 79-81.degree. (from aq. MeOH), [.alpha.]D -68.degree. (CHCl<sub>3</sub>). III (250 mg.), 2.5 cc. concd. H<sub>2</sub>SO<sub>4</sub>, and 33 cc. MeOH refluxed 5 hrs., processed in the usual manner, and the product chromatographed yielded 140 mg. IX (X = MeO), m. 77-80.degree.. IX (X = MeO) (390 mg.) in Et<sub>2</sub>O treated at room temp. with 300 mg. LiAlH<sub>4</sub> and the product passed through Al<sub>2</sub>O<sub>3</sub> yielded 60 mg. O.CMe[CHEt(OH)].CH(OMe).CH<sub>2</sub>.C.CHMe.CH<sub>2</sub>.CHMe.CH[CHMe(CH<sub>2</sub>OH)].O, m. 157-61.degree. (sublimed at 120.degree./0.001, m. 159-61.degree. with partial crystal change above 120.degree.), [.alpha.]D 118.degree.. I (2.00 g.) hydrolyzed 10 min. with HCl in the usual manner, and the crude neutral material (960 mg.) crystd. slowly from aq. MeOH gave about 100 mg. IX (X = Cl), m. 106.5-8.5.degree. (sublimed), [.alpha.]D -84.degree.. III (500 mg.) in 25 cc. EtOH

contg. 100 mg. 5% Pd-C hydrogenated 10 min. at ambient conditions and the crude product (480 mg.) recrystd. several times from C<sub>6</sub>H<sub>6</sub>-pentane gave O.CHEt.CMe(OH).CH<sub>2</sub>.CH<sub>2</sub>.CO.CHMe.CH<sub>2</sub>.CHMe.CHR.CHMe.CO (X) (R = OH), colorless crystals, m. 136-43.degree., [.alpha.]D 2.degree. (dioxane), .+-0.degree. (MeOH). X (R = OH) (70 mg.) in 3 cc. MeOH and 3 drops concd. H<sub>2</sub>SO<sub>4</sub> kept 2 hrs. at room temp., dild. with 10 cc. H<sub>2</sub>O, and cooled with Dry Ice gave 42 mg. IX (X = H), m. 51-2.degree., [.alpha.] D -142.degree. (dioxane). X (R = OH) in 2 cc. dioxane had a specific rotation of 1.degree. which dropped to -140.degree. in 4 min. after the addn. of 2 drops concd. H<sub>2</sub>SO<sub>4</sub>; the specific rotation of III remained unchanged during 8 hrs. under the same conditions. The rotatory dispersion data for the various products were given.

CC 10 (Organic Chemistry)

IT 2-Pentanone, 3-hydroxy-, 7-carboxy-3-hydroxy-2,4-dimethylheptanoate, .delta.-lactone

8-Tridecenoic acid, 3,10,11-trihydroxy-2,4,6,10-tetramethyl-7-oxo-, 3-acetate

Methynolide, dehydro-

Valeric acid, 2,3-dihydroxy-2-methyl-, 3-ester with 3-hydroxy-2,4,6-trimethylheptanedioic acid .delta.-lactone

IT Pyran-3-ol, 2-[1-(1-carboxyethyl)-8,9-dihydroxy-2,4,8-trimethyl-5-oxo-6-undecenyloxy]-4-dimethylaminotetrahydro-6-methyl-, .kappa.-lactone

(as structure of methymycin)

IT 945-06-2, Heptanedioic acid, 3-hydroxy-2,4,6-trimethyl-, .delta.-lactone

(and its esters)

IT 13083-78-8, 8-Tridecenoic acid, 3-(4-dimethylaminotetrahydro-3-hydroxy-6-methylpyran-2-yloxy)-10,11-dihydroxy-2,4,6,10-tetramethyl-7-oxo-, .kappa.-lactone

(as structure of methymycin)

IT 534-32-7, 8-Tridecenoic acid, 3,10,11-trihydroxy-2,4,6,10-tetramethyl-7-oxo-, .kappa.-lactone 100706-54-5, Carbazic acid, 2-[2-(methylthio)ethyl]-3-o-nitrobenzylidene-, ethyl ester 101885-39-6, 1,6-Dioxaspiro[4.5]decane-7-ethanol, 2-(1-hydroxypropyl)-3-methoxy-.alpha., 2,8,10-tetramethyl-107621-21-6, 8-Tridecenoic acid, 10,11-dihydroxy-2,4,6,10-tetramethyl-3,7-dioxo-, .kappa.-lactone 109157-39-3, Tridecanoic acid, 3,10,11-trihydroxy-2,4,6,10-tetramethyl-7-oxo-, .kappa.-lactone

(prepn. of)

L35 ANSWER 14 OF 20 HCA COPYRIGHT 2005 ACS on STN

50:32106 Original Reference No. 50:6449g-i,6450a-i,6451a-e Ketene acetals. XXXV. Cyclic ketene acetals and orthoesters from 2,2-dimethoxy-2,3-dihydropyran. McElvain, S. M.; McKay, G. Robert,



Jr. (Univ. of Wisconsin, Madison). Journal of the American Chemical Society, 77, 5601-5 (Unavailable) 1955. CODEN: JACSAT. ISSN: 0002-7863. OTHER SOURCES: CASREACT 50:32106.

AB 2,2-Dimethoxy-2,3-dihydroxy-2H-pyran (I) has been dealcoholated to the unstable 2-methoxy-2H-pyran (II) and also converted to 2-methoxy-5,6-dihydro-2H-pyran (III). Some reactions of III are described; of particular interest is the addn. of acrolein (IV) to produce 1-methoxy-2,10-dioxabicyclo [4.4.0]dec-3-ene (V) which was converted via hydrogenation and dealcoholation to 2,10-dioxabicyclo[4.4.0]decane (VI). VI added IV to yield, after hydrogenation 2,10,11-trioxatricyclo[4.4.4.0]tetradecane (VII). VII and the corresponding normal ester, .alpha.,.alpha.-bis(3-hydroxypropyl)-.delta.-valerolactone (VIII), are readily interconvertible. Na (138 g.) added slowly with stirring to 3 l. Me<sub>2</sub>C(OH)Ph at 140.degree., the soln. heated to 180.degree., treated dropwise (added beneath the surface) with 616 g. ClCH<sub>2</sub>CH(OMe)<sub>2</sub> (IX) at 175-85.degree., the **distillate** recycled into the mixt., and the resulting product redistd. gave 231 g. CH<sub>2</sub>:C(OMe)<sub>2</sub>, b. 89-91.degree., n<sub>D</sub><sup>25</sup> 1.4045; the residual material in the reaction flask washed with H<sub>2</sub>O, dried, and **distd.** gave PhCHMe<sub>2</sub>, b<sub>35</sub> 50-1.degree., b<sub>737</sub> 150.degree., n<sub>D</sub><sup>25</sup> 1.4887. After **distn.** of the main fraction of Me<sub>2</sub>C(OH)Ph, b<sub>32</sub> 65-80.degree., a higher boiling product, probably PhMe<sub>2</sub>COCH<sub>2</sub>CH(OMe)<sub>2</sub>, b<sub>0.6</sub> 86-7.degree., n<sub>D</sub><sup>25</sup> 1.4857, was obtained which treated with Brady's 2,4-(O<sub>2</sub>N)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NHNH<sub>2</sub> reagent gave 85% [2,4-(O<sub>2</sub>N)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NHN:CH]<sub>2</sub>, m. 315-160 (from pyridine). I (28.8 g.) and 49.2 g. sublimed (Me<sub>2</sub>CO)<sub>3</sub>Al (X) heated under N with stirring to 155.degree. and then during 1 hr. to 185.degree. to give 100% Me<sub>3</sub>COH, the mixt. cooled to 100.degree. and **distd.** at 25 mm. gave 5.6 g. II, b<sub>25</sub> 63-4.degree., n<sub>D</sub><sup>25</sup> 1.4619. II was extremely sensitive to air; it reacted vigorously with dil. HCl; it gave, treated with Brady's reagent in MeOH, the 2,4-dinitrophenylhydrazone, m. 107-8.5.degree. (from 95% EtOH), of OHC(CH<sub>2</sub>)<sub>3</sub>CO<sub>2</sub>Me. I (253 g.) hydrogenated 34 hrs. over 6 teaspoonfuls Raney Ni W-7, the mixt. centrifuged, the catalyst washed with dry Et<sub>2</sub>O, and the combined product and washings **distd.** yielded 243 g. 2,2-dimethoxytetrahydropyran (XI), b<sub>20</sub> 69-70.degree., b<sub>739</sub> 164.5-65.degree., n<sub>D</sub><sup>25</sup> 1.4298, d<sub>25</sub> 1.029; with 10% Pd-C as the catalyst no XI was obtained in a similar run; with dry dioxane the yield of XI was 40%. The hydrogenolysis portion of the mixt., HO(CH<sub>2</sub>)<sub>4</sub>CH(OMe)<sub>2</sub>, b<sub>34</sub> 112-13.degree., (0.311 g.) in MeOH treated with Brady's reagent yielded 0.522 g. 2,4-(O<sub>2</sub>N)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NHN:CH(CH<sub>2</sub>)<sub>4</sub>OH, m. 109.5-10.5.degree.. XI (29.2 g.) and 49.2 g. X heated with stirring to 140-5.degree. and then during 1 hr. to 185.degree. yielded 100% Me<sub>3</sub>COH, b. 82-3.degree., n<sub>D</sub><sup>25</sup> 1.3857; the residual mixt. cooled to 100.degree. and then **distd.** yielded 19.3 g. III, b<sub>34</sub> 70-70.5.degree., b<sub>741</sub> 153.5-4.5.degree., n<sub>D</sub><sup>25</sup> 1.4555, d<sub>25</sub> 1.023, MRD 30.29. XI (2.5 moles) dealcoholated with unsublimed

X gave only 54.5% III. III reacted vigorously with dil. HCl and Br in CCl<sub>4</sub>. III (7.1 g.) and 0.5 cc. H<sub>2</sub>O treated with a few drops dil. HCl yielded 5.2 g.  $\delta$ -valerolactone (XII), b<sub>13</sub>-14 108-9.5.degree., b<sub>740</sub> 224-6.degree., n<sub>D20</sub> 1.4557. XI hydrolyzed gave a similar yield of XII. The ester mixt. from the hydrolysis of both III and XI was converted by the method of Coffman (C.A. 29, 7938.7) to HO(CH<sub>2</sub>)<sub>4</sub>CONHNH<sub>2</sub>, m. 107-8.degree.. III (6.3 g.) and 9.4 g. PhCH<sub>2</sub>Br heated with stirring at 150.degree. for 2 hrs. and the mixt. **distd.** gave the following fractions: (1) 3.9 g., b<sub>13</sub> 82-90.degree., n<sub>D25</sub> 1.4860; (2) 1.0 g., b<sub>13</sub> 90-130.degree., n<sub>D25</sub> 1.4654; (3) 2.35 g., b<sub>1</sub> 145-9.degree., n<sub>D25</sub> 1.5253; (4) 5.05 g., b<sub>1.3</sub> 196-8.degree.; and in the cold trap 2.2 g. MeBr; fraction 4 recrystd. from EtOH yielded 3.25 g.  $\alpha$ , $\alpha$ -dibenzyl- $\delta$ -valerolactone (XIII), m. 106.5-107.degree.; the mother liquors evapd. in vacuo and the residual oil evaporatively **distd.** gave a mixt. of 1.15 g. XIII and 0.65 g. Br(CH<sub>2</sub>)<sub>3</sub>C(CH<sub>2</sub>Ph)<sub>2</sub>CO<sub>2</sub>Me; fraction 3 contained 1.7 g. Br(CH<sub>2</sub>)<sub>3</sub>CH(CH<sub>2</sub>Ph)CO<sub>2</sub>Me and 0.65 g.  $\alpha$ -benzyl- $\delta$ -valerolactone. III (57.0 g.) heated 15 hrs. at 100.degree. with 30.0 g. IV and the pale yellow mixt. fractionated yielded 4.7 g. unchanged IV, 54.4 g. V, b<sub>20</sub> 99.degree., b<sub>36</sub> 111-12.degree., n<sub>D25</sub> 1.4727, d<sub>25</sub> 1.106, and 26.5 g. pot residue. IX (275 g.) shaken with 2 tablespoonfuls W-7 Raney Ni 36 hrs. under H and the mixt. worked up in the usual manner gave 268 g. **decane** analog (XIV) of V, b<sub>0.1</sub> 38.degree., n<sub>D25</sub> 1.4653, d<sub>25</sub> 1.087; it is insol. in H<sub>2</sub>O but dissolves exothermically in dil. HCl. XIV (13.3 g.) and 25.0 g. X gave in the usual manner at 145-85.degree. 9.20 g. VI, b<sub>22</sub> 108-9.degree., b<sub>8</sub> 90-1.degree., n<sub>D25</sub> 1.4913, d<sub>25</sub> 1.091. A small amt. VI hydrolyzed with a few drops dil. HCl and the product **distd.** evaporatively gave  $\alpha$ -benzyl- $\alpha$ -(3-bromopropyl)- $\delta$ -valerolactone (XV), b<sub>0.1</sub> 140.degree.; it gave treated with p-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>COCl  $\alpha$ -[3-(p-nitrobenzoyl)propyl]- $\delta$ -valerolactone, m. 108-9.5.degree. (from ligroine, b. 90-100.degree.). VI (7.0 g.) and 8.55 g. PhCH<sub>2</sub>Br heated 10 hrs. at 110.degree. and the viscous yellow reaction mixt. **distd.** gave 1.0 g. forerun, b<sub>13</sub> 50-80.degree., and 13.3 g. XV, b<sub>0.03</sub> 159-60.degree., n<sub>D25</sub> 1.5561. VI (7.0 g.) and 8.3 g. BrCH<sub>2</sub>CO<sub>2</sub>Et heated 16.5 hrs. at 140.degree. and the mixt. **distd.** gave 2.3 g. forerun, b<sub>13</sub> 55-60.degree., and 10.3 g.  $\alpha$ -carbethoxymethyl- $\alpha$ -(3-bromopropyl)- $\delta$ -valerolactone, b<sub>0.05</sub> 153-4.degree., n<sub>D25</sub> 1.4990. VI (2.33 g.) in 50 cc. abs. EtOAc treated with ozone-contg. O at -70.degree. until a blue color persisted, the cold mixt. treated with 2.5 g. 6% Pd-SrCO<sub>3</sub>, shaken at 40 lb. pressure with H until the peroxides disappeared, centrifuged, and **distd.** yielded 0.94 g. 4-oxo-1,7-heptanediol carbonate (XVI), b<sub>0.06</sub> 94.5-5.5.degree., n<sub>D25</sub> 1.4755; and a higher boiling, unidentified material. XVI treated with 2,4-(O<sub>2</sub>N)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NHNH<sub>2</sub> gave an orange 2,4-dinitrophenylhydrazone, m. 253-4.degree. (from EtOAc). VI (18.0

g.) in 10 cc. abs. MeOH treated with a drop concd. HCl on the bulb of the thermometer caused a temp. rise to 90.degree. in 10 sec.; the excess MeOH removed and the residue **distd.** gave 19.7 g. orthoester, probably the trans isomer (XVII) of XIV, b0.1 41.5.degree., n<sub>D</sub>25 1.4663, d<sub>25</sub> 1.091. Both XVII and XIV dealcoholated with X gave about 85% VI. VI (5.80 g.) in 40 cc. dry CCl<sub>4</sub> treated at room temp. dropwise with 6.97 g. Br in 32.0 g. dry CCl<sub>4</sub> and the solvent removed in vacuo gave .alpha.-bromo-.alpha.-(3-bromopropyl)-.delta.-valerolactone (XVIIa), b0.2 160-2.degree. (decompn.). VI (1.40 g.) in 5 cc. CCl<sub>4</sub> added slowly with stirring to 3.20 g. Br in 60 cc. CCl<sub>4</sub> at -20.degree., the yellow ppt. (XVIII) filtered through a filter stick, the CCl<sub>4</sub> filtrate and the solid residue treated separately with 25 cc. H<sub>2</sub>O and then with 20 g. KI in 30 cc. H<sub>2</sub>O, and the liberated iodine titrated with aq. Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> indicated that the pptd. XVIII contained 47% of the original Br and the CCl<sub>4</sub> contained 5% unreacted Br. The stirred slurry of the resulting XVIII in another run at -20.degree. treated with a 2nd equiv. VI gave XVIIa. VI (8.70 g.) and 3.92 g. IV heated 15 hrs. at 150.degree., and the pale yellow mixt. **distd.** gave 9.65 g. 2,10,11-trioxatricyclo[4.4.4.01,6]tetradec-3-ene (XIX), b0.2 90-1.degree., m. 82.5-84.degree.; and 2.1 g. pot residue. XIX treated with Br in CCl<sub>4</sub> gave a dibromide, which decompd. to a brown oil on attempted isolation. XIX was H<sub>2</sub>O-insol. but became sol. on long standing or on heating with dil. HCl. XIX (16.9 g.) in 50 cc. dry Et<sub>2</sub>O hydrogenated 33 hrs. over 1 teaspoonful Raney Ni W-7 yielded 16.3 g. VII, m. 111-13.degree., which recrystd. from petr. ether (b. 60-8.degree.) and sublimed at 100.degree. and 0.1 mm. yielded 15.2 g. pure VII, m. 116-17.degree.; it became H<sub>2</sub>O-sol. on long standing or on heating with dil. HCl. VII hydrolyzed gave VIII; the resulting VIII contained crystals of VII and was never obtained in sufficient purity for analysis. VII (0.501 g.) added to 40 cc. H<sub>2</sub>O (acidified with a trace of concd. H<sub>2</sub>SO<sub>4</sub>), the mixt. refluxed 24 hrs. and steam **distd.**, the **distillate** (300 cc.) evapd., the remaining H<sub>2</sub>O removed by **azeotropic distn.** with C<sub>6</sub>H<sub>6</sub>, and the residual viscous VIII heated at 100.degree. and 0.1 mm. gave 0.336 g. VII as sublimate; evapn. of the 300 cc. **distillate** at room temp. and atm. pressure left no trace of VII. VII (0.500 g.) in 30 cc. dry Et<sub>2</sub>O treated with 70 cc. satd. HBr in dry Et<sub>2</sub>O, the mixt. allowed to stand overnight, the Et<sub>2</sub>O and HBr evapd. in an air stream to approx. 30 cc., the residue shaken with H<sub>2</sub>O, and evapd., and the remaining oil dissolved in hot ligroine (b. 60-8.degree.) and cooled deposited 0.561 g. (BrCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>CCO<sub>2</sub>H, colorless crystals, m. 93-4.degree..

CC 10 (Organic Chemistry)  
IT 1,3-Dioxecane-2,7-dione  
1,3-Dioxecane-2,7-dione, 7-(2,4-dinitrophenylhydrazone)  
2,10,11-Trioxatricyclo[4.4.4.01,6]-3-tetradecene  
2,10,11-Trioxatricyclo[4.4.4.01,6]tetradecane, 3,4-dibromo-

2H,5H-Pyrano[2,3-b]pyran, 3,4,4a,8a-tetrahydro-8a-methoxy-  
 2H,5H-Pyrano[2,3-b]pyran, 3,4,6,7-tetrahydro-  
 4-Heptanone, 1,7-dihydroxy-, cyclic carbonate  
 4-Heptanone, 1,7-dihydroxy-, cyclic carbonate, 2,4-  
 dinitrophenylhydrazone  
 8a,4a-(Epoxypropano)-2H,5H-pyrano[2,3-b]pyran, 6,7-dibromotetrahydro-  
 Carbonic acid, 4-oxoheptamethylene ester  
 Carbonic acid, 4-oxoheptamethylene ester, 2,4-dinitrophenylhydrazone  
 Ethylene, 1,1-dimethoxy-  
 Hydrocinnamic acid, .alpha.-(3-bromopropyl)-, methyl ester  
 Hydrocinnamic acid, .alpha.-(3-bromopropyl)-.alpha.-(3-  
 hydroxypropyl)-, .delta.-**lactone**  
 Ortho-4-pentenoic acid, 5-hydroxy-2-(3-hydroxypropyl)-, di-.delta.-  
**lactone**, Me ester  
 Orthovaleric acid, 4,5-dibromo-5-hydroxy-2,2-bis(3-hydroxypropyl)-,  
 tri-.delta.-**lactone**  
 Pyran, tetrahydro-2,2-dimethoxy-  
 Succinic acid, 2-(3-bromopropyl)-2-(3-hydroxypropyl)-, .delta.-  
**lactone**, Et ester  
 Valeric acid, 2,2-dibenzyl-5-bromo-, methyl ester  
 Valeric acid, 2,2-dibenzyl-5-hydroxy-, .delta.-**lactone**  
 Valeric acid, 2-bromo-2-(3-bromopropyl)-5-hydroxy-, .delta.-  
**lactone**  
 Valeric acid, 5-bromo-2,2-bis(3-bromopropyl)-  
 Valeric acid, 5-hydroxy-2,2-bis(3-hydroxypropyl)-, .delta.-  
**lactone**  
 Valeric acid, 5-hydroxy-2-(3-hydroxypropyl)-, .delta.-  
**lactone**, p-nitrobenzoate  
 IT 86290-14-4, Ortho-4-pentenoic acid, 5-hydroxy-, .delta.-  
**lactone**, di-Me ester  
 (alc. removal from)  
 IT 98-82-8, Cumene 617-94-7, Benzyl alcohol, .alpha.,.alpha.-dimethyl-  
 1177-16-8, Glyoxal, bis(2,4-dinitrophenylhydrazone) 3638-33-3,  
 Valeraldehyde, 5-hydroxy-, 2,4-dinitrophenylhydrazone 6026-86-4,  
 Glutaraldehydic acid, methyl ester 7092-68-4, Ortho-4-pentenoic  
 acid, 5-hydroxy-2,2-bis(3-hydroxypropyl)-, tri-.delta.-  
**lactone** 7092-68-4, 8a,4a-(Epoxypropano)-2H,5H-pyrano[2,3-  
 b]pyran, 3,4-dihydro- 7092-69-5, 2,10,11-  
 Trioxatricyclo[4.4.4.01,6]tetradecane 7092-69-5, Orthovaleric  
 acid, 5-hydroxy-2,2-bis(3-hydroxypropyl)-, tri-.delta.-  
**lactone** 32821-74-2, Hydrocinnamic acid,  
 .alpha.-(3-hydroxypropyl)-, .delta.-**lactone** 53066-10-7,  
 Acetaldehyde, (.alpha.,.alpha.-dimethylbenzyloxy)-, dimethyl acetal  
 53066-10-7, Ethane, 2-(.alpha.,.alpha.-dimethylbenzyloxy)-1,1-  
 dimethoxy- 57262-56-3, Glutaraldehydic acid, methyl ester,  
 2,4-dinitrophenylhydrazone 66607-28-1, Orthovaleric acid,  
 5-hydroxy-, .delta.-**lactone**, di-Me ester 79898-65-0,  
 Valeraldehyde, 5-hydroxy-, dimethyl acetal 99469-47-3,

2H,5H-Pyrano[2,3-b]pyran, hexahydro-8a-methoxy-, cis- 99469-48-4,  
 2H,5H-Pyrano[2,3-b]pyran, hexahydro-8a-methoxy-, trans-  
 104394-98-1, Orthovaleric acid, 5-hydroxy-2-(3-hydroxypropyl)-,  
 di-.delta.-**lactone**, Me ester, trans- 104394-98-1,  
 Orthovaleric acid, 5-hydroxy-2-(3-hydroxypropyl)-, di-.delta.-  
**lactone**, Me ester, cis- 122735-65-3, 2H-Pyran,  
 3,4-dihydro-6-methoxy- 408538-13-6, 4H-Pyran, 2-methoxy-  
 (prepn. of)

IT 13392-69-3, Valeric acid, 5-hydroxy-  
 (.delta.-**lactone** and other derivs.)

L35 ANSWER 15 OF 20 HCA COPYRIGHT 2005 ACS on STN

49:73373 Original Reference No. 49:13883c-i,13884a-i,13885a-i,13886a-f  
 Oxidation products of diisobutylene. III. Products from ring opening  
 of 1,2-epoxy-2,4,4-trimethylpentane. Graham, A. R.; Millidge, A.  
 F.; Young, D. P. (Distillers Co. Ltd., Epsom, UK). Journal of the  
 Chemical Society, Abstracts 2180-2200 (Unavailable) 1954. CODEN:  
 JCSAAZ. ISSN: 0590-9791.

GI For diagram(s), see printed CA Issue.

AB cf. Hickinbottom, C.A. 43, 1309h. VII (320 g.) and 1 l. 0.1N H2SO4  
 stirred 5 h. with the temp. kept below 35.degree., and the whole  
 warmed to 35.degree. to liquefy the product, which was sepd. (the  
 dil. H2SO4 layer was recycled in subsequent expts.), and  
**distd.**, gave about 238 g. II, b10 105-10.degree., m.  
 55-7.degree.; the lower-boiling material (50 g.) consisted of  
 unchanged VII, XVI, and unsatd. alcs. (XXIVA). The following  
 summarizes expts. carried out to show the effects of the concn. and  
 kind of acid and of time (in hrs.) on the yields of VII plus XVI,  
 XXIVA, II, and condensation products (b10 112-30.degree.): N H2SO4,  
 3, 6, 18, 40, 0; 0.2N H2SO4, 5, 0, 25, 51, 0; 0.1N H2SO4, 5.25, 4,  
 16, 71, 0; 0.05N H2SO4, 5, 8, 12, 61, 0; 0.02N H2SO4, 5, 26, 9, 43,  
 0; 0.01N H2SO4, 10, 40, 3, 33, 0; 0.1N HCl, 5, 0, 27, 30, 32; 0.01N  
 HNO3, 5, 0, 6, 75, 0; 0.1N H2SO4 dild. with half its vol. of EtOH,  
 5, -, -, 75, 0. IX (32 g.) shaken 12 h. at room temp. with 100 mL.  
 0.1N H2SO4 gave 23.2 g. diol, b10 90-2.degree.. VII and N NaOH  
 refluxed 66 h. gave only a trace of II; VII (64 g.) and 200 mL. N  
 NaOH heated 2.5 h. at 200.degree. in a Baskerville-Lindsay autoclave  
 with reciprocating stirrer, and the org. product sepd. and  
**distd.** gave 76% II; 2N Na2CO3 in place of the NaOH gave 76%  
 II. VII (32 II. g.), 100 mL. H2O, and 20 mL. EtOH refluxed 3 h.  
 gave 35% VII and 25% AcOH gave presumably dihydro-4-methyl-4-  
 neopentyl-2-(1,3,3-trimethylbutyl)-1,3-dioxole (XXIVB) (cf. C.A. 44,  
 3888g). Styrene oxide (6 g.) and 10 mL. N NaOH at 175.degree. gave  
 2.2 g. PhCH(OH)CH2OH, b12 155-65.degree., m. 62-4.degree. (from  
 XII); similarly, PhCMe.CH2.O gave PhCMe(OH)CH2OH, b10  
 144-50.degree., m. 44-6.degree. (from XII-petr. ether). II had the  
 following temp.-vapor pressure values: 20.degree., 0.3;  
 118.7.degree., 20; 134.3.degree., 40; 143.8.degree., 60;

157.1.degree., 100; 175.1.degree., 200; 196.8.degree., 400; and 219.8.degree. (decompn.) 760 mm. II (20 g.), 150 mL. XII, and a drop of H<sub>2</sub>SO<sub>4</sub> refluxed, the H<sub>2</sub>O, which was formed immediately removed continuously, and the XII soln. washed and **distd.** gave 100% XXIVB, b<sub>10</sub> 132.degree., n<sub>20D</sub> 1.4408. II and a trace of H<sub>2</sub>SO<sub>4</sub> **distd.** at 15 mm. gave XXIVB, also obtained by refluxing II and N H<sub>2</sub>SO<sub>4</sub> or by mixing II and concd. HCl at room temp. To 29 g. II and 26 g. XVI in XII was added 1 drop H<sub>2</sub>SO<sub>4</sub>; an exothermic reaction occurred and H<sub>2</sub>O **distd.** as an **azeotrope** and was sepd. continuously. When no more H<sub>2</sub>O was evolved, the mixt. was washed with aq. NaOH and **distd.** from K<sub>2</sub>CO<sub>3</sub> to give 49 g. XXIVB, b<sub>10</sub> 132.degree., n<sub>20D</sub> 1.4409. With 1 drop of H<sub>3</sub>PO<sub>4</sub> as catalyst, 29.2 g. II and 16.6 g. cyclohexanone gave 19.3 g. dioxole deriv., b<sub>10</sub> 124.degree., n<sub>20D</sub> 1.4562, and II and BzH gave the dioxole deriv., b<sub>10</sub> 155-7.degree., n<sub>20D</sub> 1.4961. **Distn.** of II with H<sub>2</sub>SO<sub>4</sub> gave a complex mixt. of products. II (29 g.), 20 g. Ac<sub>2</sub>O, and 18 g. C<sub>5</sub>H<sub>5</sub>N warmed 1 h. on the steam bath gave 13.5 g. monoacetate (XXV), b<sub>10</sub> 108.5-10.degree., n<sub>20D</sub> 1.4413; the diacetate, prep'd. by the Hickinbottom method (C.A. 43, 1309h), b<sub>12</sub> 120.degree., n<sub>20D</sub> 1.4341. VII (100 g.) added slowly to 1.2 g. H<sub>2</sub>SO<sub>4</sub> in 500 mL. EtOH with the temp. held below 45.degree., the whole kept overnight, the pH adjusted to 9 with aq. NaOH, and the mixt. **distd.** gave Me<sub>3</sub>CCH<sub>2</sub>CMe(OEt)CH<sub>2</sub>OH (XXVI) [contg. about 8% of presumably Me<sub>3</sub>CCH<sub>2</sub>CHMeCH(OEt)<sub>2</sub>], b<sub>12</sub> 94-7.degree.. BF<sub>3</sub>.Et<sub>2</sub>O (XXVII) in place of the H<sub>2</sub>SO<sub>4</sub> in the above expt. gave pure XXVI, b<sub>10</sub> 92-3.degree., n<sub>20D</sub> 1.4403, d<sub>20</sub> 0.8994; 3,5-dinitrobenzoate, m. 89-90.degree. (from EtOH). VII, MeOH, and XXVII as above gave 62% Me<sub>3</sub>CCH<sub>2</sub>CMe(OMe)CH<sub>2</sub>OH (XXVIII), b<sub>12</sub> 90-3.5.degree., d<sub>20</sub> 0.9129, n<sub>20D</sub> 1.4433 (3,5-dinitrobenzoate, m. 74-5.degree.); the XXVII must be destroyed by the addn. of aq. NaOH before **distn.** of the XXVIII. With H<sub>2</sub>SO<sub>4</sub> in place of XXVII the yield of XXVIII was 47%, and no acetal was detected. VII, iso-PrOH, and H<sub>2</sub>SO<sub>4</sub> gave no product; VII, BuOH, and H<sub>2</sub>SO<sub>4</sub> gave Me<sub>3</sub>CCH<sub>2</sub>CMe(OBu)CH<sub>2</sub>OH, b<sub>10</sub> 114-19.degree., d<sub>20</sub> 0.8802, n<sub>20D</sub> 1.4408 (3,5-dinitrobenzoate, m. 66-7.degree.); VII, (HOCH<sub>2</sub>)<sub>2</sub>, and XXVII gave 42% Me<sub>3</sub>CCH<sub>2</sub>CMe(OCH<sub>2</sub>CH<sub>2</sub>OH)CH<sub>2</sub>OH (XXIX), b<sub>0.5</sub> 112-16.degree., n<sub>20D</sub> 1.4597, [bis(3,5-dinitrobenzoate), m. 107-9.degree. (from Me<sub>2</sub>CO)]; XXIX (19.0 g.), 32.5 g. XVIII A, and 19.0 g. C<sub>5</sub>H<sub>5</sub>N, mixed with cooling, gave 82% diester, b<sub>24</sub> 160-4.degree., n<sub>20D</sub> 1.4472; VII, HOCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH, and XVII gave 39% Me<sub>3</sub>CCH<sub>2</sub>CMe(OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>OH)CH<sub>2</sub>OH), b<sub>0.5</sub> 134.degree., n<sub>20D</sub> 1.4623 [bis(p-nitrobenzoate), m. 65-7.degree. (from Me<sub>2</sub>CO-EtOH)]; VII, Me<sub>2</sub>C(OH)CH<sub>2</sub>CH(OH)Me, and XVII gave 11% Me<sub>3</sub>CCH<sub>2</sub>CMe[OCHMeCH<sub>2</sub>CMe<sub>2</sub>(OH)]C H<sub>2</sub>OH, b<sub>0.1</sub> 113-15.degree., n<sub>20D</sub> 1.4548; VII, (HOCH<sub>2</sub>)<sub>2</sub>CHOH, and XVII gave 31% Me<sub>3</sub>CCH<sub>2</sub>CMe[OCH<sub>2</sub>CH(OH)CH<sub>2</sub>OH]CH<sub>2</sub>OH, b<sub>0.3</sub> 154-8.degree., n<sub>20D</sub> 1.4688 [tris(p-nitrobenzoate), m. 128-30.degree. (from Me<sub>2</sub>CO EtOH)]. VII and 0.05N NaOEt did not react when refluxed for extended periods of time. VII (128 g.) added to soln. of 23 g. Na in 500 mL. EtOH, the whole refluxed 3 h., the EtOH **distd.**, the residue

washed with H<sub>2</sub>O, dissolved in Et<sub>2</sub>O, and the soln. concd. and **distd.** gave 68% Me<sub>3</sub>CCH<sub>2</sub>CMe(OH)CH<sub>2</sub>OEt (XXX), b<sub>16</sub> 79.degree., d<sub>20</sub> 0.8693, n<sub>20D</sub> 1.4277, 3,5-dinitrobenzoate, m. 48-50.degree.; acetate, b<sub>10</sub> 92.degree., n<sub>20D</sub> 1.4263. An equiv. amt. of NaOH in EtOH with VII gave 61-66 % XXX. NaOMe in refluxing MeOH with VII gave 51% Me<sub>3</sub>CCH<sub>2</sub>CMe(OH)CH<sub>2</sub>OMe, b<sub>10</sub> 65-6.degree., d<sub>20</sub> 0.8802, n<sub>20D</sub> 1.4294 (3,5-dinitrobenzoate, m. 68.degree.); iso-PrONa in iso-PrOH gave 7.5% Me<sub>3</sub>CCH<sub>2</sub>CMe(OH)CH<sub>2</sub>OCHMe<sub>2</sub>, b<sub>10</sub> 79-83.degree., d<sub>20</sub> 0.8608, n<sub>20D</sub> 1.4272; VII, BuOH, and 1 mol NaOH gave 65% Me<sub>3</sub>CCH<sub>2</sub>CMe(OH)CH<sub>2</sub>OBu, b<sub>10</sub> 100-4.degree., d<sub>20</sub> 0.8668, n<sub>20D</sub> 1.4335. VII (64 g.), 200 g. Me(CH<sub>2</sub>)<sub>11</sub>OH, and 10 g. NaOH heated 2 h. at 175.degree. gave a small yield of 1-dodecyloxy compd., b<sub>0.5</sub> 168-80.degree., n<sub>20D</sub> 1.4474; under the same conditions as in the previous example, 128 g. VII, 150 g. (HOCH<sub>2</sub>)<sub>2</sub>, and 8 g. NaOH gave 46% 1-(2-hydroxyethoxy) deriv., b<sub>0.3</sub> 94-100.degree., n<sub>20D</sub> 1.4541; 47 g. PhOH and 20 g. NaOH in 40 mL. EtOH and 50 mL. H<sub>2</sub>O refluxed 8 h. with 64 g. VII gave 44% 1-phenoxy deriv., b<sub>10</sub> 148-53.degree., n<sub>20D</sub> 1.4993 (3,5-dinitrobenzoate, m. 88-90.degree.); and 2-C<sub>10</sub>H<sub>7</sub>OH gave 19% corresponding 1-(2-naphthoxy) deriv., b<sub>0.003</sub> 136-40.degree., needles, m. 46-7.degree.. Both XXVI and XXX, refluxed in EtOH contg. a trace of H<sub>2</sub>SO<sub>4</sub>, were unchanged; when **distd.** from I, both compds. gave 85% XVI. Shaking XXX with concd. HCl gave 41% XVI. XXX (18 g.), 32 g. KMnO<sub>4</sub>, and 40 g. NaOH in 500 mL. H<sub>2</sub>O heated on the steam bath, the MnO<sub>2</sub> and neutral products filtered off, and the filtrate acidified gave 1.8 g. Me<sub>3</sub>CCH<sub>2</sub>CMe(OH)CO<sub>2</sub>H (XXXI), m. 107-8.degree.; XXVI treated similarly also gave XXXI. IIA (57 g.) in 300 mL. MeOH added to 40 g. KCN in 100 cc. H<sub>2</sub>O, then 30 g. H<sub>2</sub>SO<sub>4</sub> in 100 mL. H<sub>2</sub>O added dropwise with stirring, the whole kept 2 h., dild. with 2 vols. H<sub>2</sub>O, extd. with Et<sub>2</sub>O, and the exts. concd. and **distd.** gave unchanged IIA and 5 g. presumably of cyanohydrin (XXXII), b<sub>20</sub> 110-17.degree., n<sub>20D</sub> 1.432; 2 g. XXXII and concd. HCl refluxed 2 h. gave 0.34 g. XXXI. VII (256 g.) and 1.5 l. aq. NH<sub>3</sub> (d. 0.88) heated 5 h. at 190.degree. in a steel autoclave, the whole cooled, extd. with CHCl<sub>3</sub>, and the exts. washed with a little H<sub>2</sub>O, dried, concd., and **distd.** gave Me<sub>3</sub>CCH<sub>2</sub>CMe(OH)CH<sub>2</sub>NH<sub>2</sub> (XXXIII), b<sub>14</sub> 87-8.degree., n<sub>20D</sub> 1.4580, d<sub>2020</sub> 0.8991, K<sub>b</sub> 4.5 .times. 10<sup>-5</sup> [picrate, orange plates, m. 151-2.degree. (from EtOH); HCl salt, plates, m. 183.degree. (from EtOH-Et<sub>2</sub>O)], and (Me<sub>3</sub>CCH<sub>2</sub>CMe(OH)CH<sub>2</sub>)<sub>2</sub>NH (XXXIV), b<sub>1</sub> 130-2.degree., n<sub>20D</sub> 1.4619, d. 0.9088 [picrate, long prisms, m. 154-5.degree.; sulfate, prisms, m. 228-9.degree. (from H<sub>2</sub>O contg. a little EtOH); carbonate, laths, m. 204.degree. (from EtOH-Et<sub>2</sub>O)]. From 512 g. VII and 1050 mL. aq. NH<sub>3</sub> (d. 0.88) heated 5 h. at 158-60.degree. (max. pressure 31 atm.), the whole refluxed to remove the NH<sub>3</sub>, cooled, 250 g. NaCl added, the mixt. extd. with 500 and 100 mL. PhMe, and the exts. concd. and **distd.** gave 313 g. XXXIII and 166 g. XXXIV; 128 g. VII and 300 mL. 3.5N EtOH-NH<sub>3</sub> heated 4 h. at 180.degree. gave 66% XXXIV. A byproduct from these reactions of VII and NH<sub>3</sub> was not identified but

appeared to be a compd.  $C_{12}H_{17}NO$ , b14 129-30.degree., n20D 1.4535, which formed a 3,5-dinitrobenzoate, m. 131-2.degree. (from EtOH and then petr. ether). The effect of the  $NH_3$ -VII molar ratio on the yield of XXXIII and XXXIV is summarized as follows ( $NH_3$ -VII molar ratio, % XXXIII, % XXXIV): 1.15, 9, 71.5; 4.25, 51.5, 34.0; 5.0, 54, 30; 6.75, 57, 26; 15, 63, 9; and 67, 63, trace. XXXIII (20 g.) and 100 mL. concd. HCl refluxed 2 h., the whole cooled, the oily product extd. into Et2O, and the exts. concd. and **distd.** gave 6.9 g. 95% pure XVI; the HCl layer made alk. with NaOH gave 18% either or both  $Me_3CCH_2C(:CH_2)CH_2NH_2$  or  $Me_3CCH:CHCH_2NH_2$ , b13 51-3.degree., n20D 1.4488, since 1 M H was absorbed over Adams catalyst to give XXIX. To 16.5 g. XXXIII, 20 g.  $NaHCO_3$ , 200 mL.  $H_2O$ , and 150 mL. Et2O, cooled in ice, was added 17 g.  $BzCl$  dropwise; a white solid sepd. but redissolved on the addn. of  $CHCl_3$ ; the org. layer washed with dil. NaOH, dil.  $H_2SO_4$ , dried, concd., and the residue, triturated with Et2O, gave 23 g.  $Me_3CCH_2CMe(OH)CH_2NHBz$ , laths, m. 103-5.degree. (from  $CHCl_3$ -petr. ether). XXXIII (22 g.) and 22 g. Ac2O reacted exothermally; the whole kept 1 h., poured into  $H_2O$ , the neutral product extd. into Et2O, and the exts. concd. and **distd.** gave 3 g. impure 4,5-dihydro-2,5-dimethyl-5-neopentyloxazole, b14 70-6.degree., n20D 1.4422 (picrate, m. 126.degree.), and 2.5 g. unidentified nonbasic material (C 68.8, H 11.0, N 7.4%), b14 135-40.degree., n20D 1.4695. VII (128 g.), 70 g. 33% EtOH-MeNH2, and 250 mL. EtOH heated 5 h. at 180.degree. gave  $Me_3CCH_2CMe(OH)CH_2NHMe$ , b14 82.degree., n20D 1.4461, Kb 8 .times. 10-4 (picrate, yellow prisms, m. 129-30.degree.), and  $[Me_3CCH_2CMe(OH)CH_2]_2NMe$  (XXXV), waxy solid which could not be recrystd. (b15 160-80.degree.); HCl salt (XXXVI), m. 169-72 (from EtOH-Et2O). From XXXVI in the usual manner was obtained XXXV, m. 42-3.degree.; [HBr salt (XXXVII), m. 198.degree. (from aq. EtOH)]; from XXXVII was regenerated XXXV, m. 66.degree.. Et2NH (320 mL.), 300 mL. EtOH, and 256 g. VII heated 5 h. at 160.degree. gave  $Me_3CCH_2CMe(OH)CH_2NEt_2$  (XXXVIII), b15 95-6.degree., b756 220.degree., n20D 1.4401, Kb 5 .times. 10-6 (picrate, lemon-yellow cubes, m. 105.degree.); incomplete reaction took place on heating Et2NH, EtOH, and VII at 140.degree. 3 h.; in the absence of EtOH, reaction occurred only to the extent of about 5%. XXXVIII (150 g.), 150 g. MeI, and 500 mL. MeOH heated 5 h. at 120.degree. gave 170 g. methiodide, m. 147.degree. (from EtOH-Et2O). MeBr (4 g.), 5 g. XXXVIII, and 25 g. EtOAc heated 5 h. at 130.degree. gave 4 g. methobromide, m. 124-6.degree. (from  $Me_2CO$  contg. a little Et2O). VII (128 g.) and 200 g. 33% aq.  $Me_2NH$  heated 4 h. in a stainless-steel stirred autoclave at 180.degree. gave 76%  $Me_3CCH_2CMe(OH)CH_2NMe_2$ , b14 77-8.degree., n20D 1.4370; picrate, yellow rhombs, m. 128.degree. (from EtOH); methiodide, m. 129-30.degree. (from EtOH-Et2O).  $PhNH_2$  (64 g.), 64 g. VII, and 200 mL. EtOH heated 5 h. at 170-80.degree. gave 54 g. crude  $Me_3CCH_2CMe(OH)CH_2NHPh$ , b10 150-95.degree., m. 68.degree. (after



trituration with and recrystn. from petr. ether); picrate, orange plates, m. 134-5.degree. (from EtOH). Similarly were obtained 38% Me3CCH2CMe(OH)CH2NMePh, b10 165-7.degree., n20D 1.5282; Me3CCH2CMe(OH)CH2R(R = morpholino), b12 125-6.degree., n20D 1.4633 [picrate, yellow prisms, m. 158.degree. (from MeOH); methiodide, m. 108-10.degree. (from Me2COEtOAc); methobromide, plates, m. 161-4.degree. (from Me2COMeOH)]. As with VII above, IX and NH3 gave 15% of material, b15 76-81.degree., apparently a mixt. of Me3CCH(OH)CMe2NH2 and Me3CCH(NH2)CMe2OH, which was not resolved; the mixt. gave a HCl salt, m. 222.degree. (from EtOHEt2O); in a repeat expt. was isolated what is presumed to be O.CH(CMe3).CMe2.NH.CMe2.CHCMe3 (XXXIX), b12 127-9.degree., n20D 1.4577; picrate, bright yellow crystals, m. 191.degree.. VII (30 g.) added during 2-3 min. to 200 mL. glacial AcOH contg. 1 g. H2SO4, the H2SO4 neutralized with excess NaOAc, the whole filtered, the filtrate partitioned between Et2O and H2O, and the Et2O soln. washed with aq. NaOH, concd., and **distd.** gave 3.5 g. (XL), b15 80-110.degree., n20D 1.4359, and 3.4 g. (XLI), b15 110-25.degree., n20D 1.4395. VII (64 g.), 41 g. anhyd. NaOAc, and 500 mL. AcOH refluxed 10 h. gave 7.8 g. unidentified material, b10 71-8.degree., n20D 1.4341, and 12.7 g. Me3CCH2CMe(OH)CH2OAc (XLII), b12 107.degree., n20D 1.4392, identical with XXV. II (64 g.) added to 250 mL. AcOH contg. 2 mL. XXVII gave 34.1 g. (largely XVI), and 4.9 g. (unidentified), b10 103-10.degree.. VII (64 g.) added slowly to 40 g. AcCl and 250 mL. CCl4 at the b.p. gave a mixt. of a chlorotrimethylpentene, b760 131.degree., a trimethylpentenyl acetate, b12 34-82.degree., and a trimethylchloropentyl acetate, b12 82-105.degree.. VII (32 g.) added at 0.degree. to 80 mL. 3.5N Et2O-HCl, the whole kept 2 h. at 0.degree., washed with cold H2O, and the Et2O layer dried and **distd.** gave 10.2 g. Me3CCH2CMe(OH)CH2Cl (XLIII), b13 70-1.degree., n20D 1.4519, and about 60% of higher-boiling material consisting of XVI and a Cl-contg. compd. XLIII (10 g.), 8 g. KOAc, and 20 mL. MeOH heated 16 h. at 140.degree., the whole cooled, concd., the residue dild. with H2O, the whole extd. with Et2O, and the Et2O layer concd. and **distd.** gave 2.7 g. II. XLIII (3.5 g.), 6 mL. Et2NH, and 5 mL. MeOH heated 3 h. at 160.degree., the whole cooled, dild. with Et2O, filtered, and the filtrate concd. and **distd.** gave 1.4 g. XXXVIII; similarly, XLIII and MeOH-NH3 gave 43% XXXIII. XLIII (10 g.) and anhyd. (CO2H)2 were **distd.** to give a trimethylchloropentene, b. 151-2.degree., n20D 1.4438-1.4445. XLIII (5 g.), 5 g. KMnO4, 3 g. NaOH, and 100 mL. H2O heated 4-5 h. on the steam bath, the whole filtered, and the filtrate acidified gave XXXI. VII (64 g.), 126 g. Na2SO3.7H2O, and 500 mL. H2O were heated 6 h. at 140-60.degree., the whole was cooled, washed with Et2O, and the H2O layer kept until a cryst. product (XLIV) sepd. (more was obtained by concn.); XLIV was shown to be Me3CCH2CMe(OH)CH2SO3Na.H2O, lustrous plates, m. 202.degree.

[S-benzylthiuronium salt, laths, m. 135.degree. (from aq. EtOH)]; the Et<sub>2</sub>O exts. contained IIA and II. XLIV (25 g.) and 75 mL. Ac<sub>2</sub>O refluxed 0.25 h., the whole dild. with H<sub>2</sub>O, the AcOH steam-distd. and the residue cooled gave an unsatd. sulfonate monohydrate (XLV), plates, m. 216.degree.; S-benzylthiuronium salt, m. 180-1.degree.. XLV (6 g.) hydrogenated over Adams catalyst gave Me<sub>3</sub>CCH<sub>2</sub>CHMeCH<sub>2</sub>SO<sub>3</sub>Na, indefinite m.p.; S-benzylthiuronium salt, needles, m. 151.degree. (from aq. EtOH). VII (128 g.), 68 g. 96% KCN, and 2-3 pellets KOH heated 5 h. at 130-40.degree. gave 9% Me<sub>3</sub>CCH<sub>2</sub>CMe:CHCN, b<sub>12</sub> 85-6.degree. (the IR absorption spectra had bands at 819 and 835 cm.<sup>-1</sup> characteristic of trisubstituted ethylenes), and another unidentified basic substance, C<sub>16</sub>H<sub>33</sub>NO, b<sub>14</sub> 125-32.degree., n<sub>20D</sub> 1.4525-1.4529. VII added to MeNa in EtOH gave 36% Me<sub>3</sub>CCH<sub>2</sub>CMe(OH)CH<sub>2</sub>SH (XLVI), b<sub>14</sub> 96-8.degree., n<sub>20D</sub> 1.4749; XLVI (7 g.) and 100 g. Raney Ni in 10 mL. EtOH refluxed 5 h. gave Me<sub>3</sub>CCH<sub>2</sub>CMe<sub>2</sub>OH, b. 143-5.degree., n<sub>20D</sub> 1.4238. VII (14 g.), 12.4 g. PhCH<sub>2</sub>SH, 6 g. NaOH, and 10 mL. EtOH refluxed 2.5 h. gave 19 g. Me<sub>3</sub>CCH<sub>2</sub>CMe(OH)CH<sub>2</sub>SCH<sub>2</sub>Ph, b<sub>0.1</sub> 104-5.degree., n<sub>20D</sub> 1.5290. VII and MeMgI treated in the usual manner gave a mixt. of products contg. probably Me<sub>3</sub>CCH<sub>2</sub>CHMeCHMeOH [prepd. from XVI and MeMgI, b<sub>19</sub> 75-80.degree., n<sub>20D</sub> 1.4325; 3,5-dinitrobenzoate, m. 61.degree.], and Me<sub>3</sub>CCH<sub>2</sub>CMe(OH)CH<sub>2</sub>Me. VII and AcCHNaCO<sub>2</sub>Et in dioxane heated 5 h. at 150.degree. gave a liq. (XLVII), b<sub>0.7</sub> 104-15.degree., consisting of a mixt. of products, one of which was probably AcCH.CO.O.CH<sub>2</sub>.CMeCH<sub>2</sub>CMe<sub>3</sub> (XLVIII) (2,4-dinitrophenylhydrazone, m. 114-15.degree.); XLVIII on boiling with aq. KOH gave presumably Me<sub>3</sub>CCH<sub>2</sub>CMe(CH<sub>2</sub>Ac)CH<sub>2</sub>OH, b<sub>12</sub> 105-15.degree., n<sub>20D</sub> 1.4430. VII (256 g.) and Raney Ni in EtOH hydrogenated (initial pressure 100 atm.) 2-3 h. at 110-20.degree. gave 128 g. XVII (along with some Me<sub>3</sub>CCH<sub>2</sub>CHMe<sub>2</sub> and C<sub>8</sub> olefin); VII, Raney Ni, and dioxane, plus 2 drops 40% NaOH soln., gave 60% XVII. In the vapor phase over 5% Ni on pumice at 200.degree., VII and H gave 40-50% XVII.

CC 10 (Organic Chemistry)

IT 1,3-Dioxolane, 4-methyl-4-neopentyl-2-phenyl-  
 1,4-Dioxaspiro[4.5]**decane**, 2-methyl-2-neopentyl-  
 1-Pentanol, 2-(3-hydroxy-1,3-dimethylbutoxy)-2,4,4-trimethyl-  
 1-Pentanol, 2-(3-hydroxypropoxy)-2,4,4-trimethyl-  
 1-Pentanol, 2-(3-hydroxypropoxy)-2,4,4-trimethyl-,  
     bis(p-nitrobenzoate)  
 1-Pentanol, 2-butoxy-2,4,4-trimethyl-, 3,5-dinitrobenzoate  
 1-Pentanol, 2-ethoxy-2,4,4-trimethyl-, 3,5-dinitrobenzoate  
 1-Pentanol, 2-methoxy-2,4,4-trimethyl-, 3,5-dinitrobenzoate  
 1-Propanol, 2-neopentyl-2,3'-oxydi-  
 1-Propanol, 2-neopentyl-2,3'-oxydi-, bis(p-nitrobenzoate)  
 2-Heptanone, 4-(hydroxymethyl)-4,6,6-trimethyl-  
 2-Heptanone, 4-(hydroxymethyl)-4,6,6-trimethyl-,  
     2,4-dinitrophenylhydrazone  
 2-Hexanol, 3,5,5-trimethyl-

2-Hexanol, 3,5,5-trimethyl-, 3,5-dinitrobenzoate  
 2-Oxazoline, 2,5-dimethyl-5-neopentyl-, picrate  
 2-Pentanol, 1-(benzylthio)-2,4,4-trimethyl-  
 2-Pentanol, 1-anilino-2,4,4-trimethyl-, picrate  
 2-Pentanol, 1-methoxy-2,4,4-trimethyl-, 3,5-dinitrobenzoate  
 2-Pentanol, 2,4,4-trimethyl-1-(methylthio)-  
 2-Pentanol, 2,4,4-trimethyl-1-methylamino-  
 2-Pentanol, 2,4,4-trimethyl-1-methylamino-, picrate  
 2-Pentanol, 2,4,4-trimethyl-1-phenoxy-, 3,5-dinitrobenzoate  
 2-Pentanol, 2,4,4-trimethyl-1-N-methylanilino-  
 2-Pentenylamine, 2,4,4-trimethyl-  
 Allylamine, 2-neopentyl-  
 Ammonium, (2-hydroxy-2,4,4-trimethylpentyl)trimethyl-, iodide  
 Benzamide, N-(2-hydroxy-2,4,4-trimethylpentyl)-  
 Carbonic acid, compd. with 1,1'-iminobis[2,4,4-trimethyl-2-pentanol]  
 Ethyl alcohol, compd. with 2,4-dinitrophenylhydrazones of .gamma.-  
     **lactone** of 2-acetyl-3-(hydroxymethyl)-3,5,5-  
     trimethylhexanoic acid  
 Morpholine, 2,6-di-tert-butyl-3,3,5,5-tetramethyl-  
 Morpholine, 2,6-di-tert-butyl-3,3,5,5-tetramethyl-, picrate  
 Pentene, chlorotrimethyl-  
 Pentylamine, 4,4-dimethyl-2-methylene-  
 Valeric acid, 2-hydroxy-2,4,4-trimethyl-  
 IT Hexanoic acid, 2-acetyl-3-(hydroxymethyl)-3,5,5-trimethyl-, .gamma.-  
     **lactone**  
     (and its derivs.)

L35 ANSWER 16 OF 20 HCA COPYRIGHT 2005 ACS on STN

48:60586 Original Reference No. 48:10776d-g **Esters** of  
     **cyclic** acetals. Brandner, John D. (Atlas Powder Co.). US  
 2648680 19530811 (Unavailable). APPLICATION: US

AB An alk. catalyst is used in the esterification of a fatty acid,  
 contg. 11-20 C atoms, with a cyclic acetal, contg. a free HO group,  
 while water is removed **azeotropically** as soon as it is  
 formed. [Yields given below are based on acid charged minus that  
 used in soap formation.] Thus, 9.31 moles 2-methyl-2-isobutyl-4-  
 methylol-1,3-dioxolane (I), 6.65 moles stearic acid (II), 7 g. NaOH,  
 and 80 g. iso-BuCOMe are charged into a flask provided with 2  
 Barrett receivers and an automatic stirrer; after 7-hrs. 52.6% of  
 product are obtained. Similarly, 4.81 moles I, 4.48 moles II, 19.8  
 g. NaOH, and 80 g. xylene yield 63.0% of product in 5 hrs.; 2.4  
 moles 2,2-dimethyl-4-methylol-1,3-dioxolane, 2.11 moles II, 4.4 g.  
 NaOH, and 130 g. xylene give in 11.5 hrs. 78.5% of product b3.0  
 213.degree.; 2.4 moles 2-methyl-2-ethyl analog of I, 2.11 moles II,  
 4.4 g. NaOH, and 130 g. xylene, yield after 9.5 hrs. 80.2% of  
 product b0.6 198.degree.; 1.2 moles 2-propyl-4-methylol-1,3-  
 dioxolane, 1.05 moles of II, 2.3 g. NaOH, and 56 g. xylene, yield  
 after 6 hrs. 87.7% of product b0.15 184.degree.; 6 moles

2,2-pentamethylene-4-methylol-1,3-dioxolane, 5 moles II, 12.3 g. NaOH, and 284 g. cyclohexanone yield 65.7% product in 3.5 hrs.; 1.2 moles 2,2-pentamethylene-5-methyl-5-hydroxymethyl-1,3-dioxane, 1.05 moles oleic acid, 2 g. NaOH, and 80 g. xylene yield in 6.5 hrs. 67.5% of product b0.15 213.degree..

CC 10 (Organic Chemistry)

IT 1,3-Dioxolane-4-methanol, 2,2-dimethyl-, stearate  
 1,3-Dioxolane-4-methanol, 2-ethyl-2-methyl-, stearate  
 1,3-Dioxolane-4-methanol, 2-isobutyl-2-methyl-, stearate  
 1,3-Dioxolane-4-methanol, 2-propyl-, stearate  
 1,4-Dioxaspiro[4.5]**decane**-2-methanol, stearate  
 1,5-Dioxaspiro[5.5]undecane-3-methanol, 3-methyl-, oleate  
 Oleic acid, 3-methyl-1,5-dioxaspiro[5.5]undec-3-ylmethyl ester

L35 ANSWER 17 OF 20 HCA COPYRIGHT 2005 ACS on STN

45:52776 Original Reference No. 45:8988i,8989a-i,8990a-c Preliminary syntheses in the morphine series. III. Michael condensations with 2-aryl-2-cyclohexen-1-ones and cyclization of the products to octahydrophenanthrene derivatives. Ginsburg, David; Pappo, Raphael (Weizmann Inst. Sci., Rehovoth, Israel). Journal of the Chemical Society, Abstracts 938-45 (Unavailable) 1951. CODEN: JCSAAZ. ISSN: 0590-9791. OTHER SOURCES: CASREACT 45:52776.

AB 2,3-Dimethoxyphenyl-2-cyclohexen-1-one (0.1 mol.), 0.2 mol. CH<sub>2</sub>(CO<sub>2</sub>Et)<sub>2</sub>, and 0.025 mol. 20% EtONa in EtOH, kept 3 h. at 60.degree. and overnight at room temp., treated with 0.025 mol. AcOH. and dild. with 200 mL. ether, give 95% crude Et 2-(2,3-dimethoxyphenyl)-3-ketocyclohexanemalonate (I), b0.1 220.degree. (bath), decomp. on **distn.** of large quantities; 2,4-dinitrophenylhydrazone, yellow, m. 117-19.degree.. Et 3-keto-2-phenylcyclohexanemalonate (II), an oil (2,4-dinitrophenylhydrazone, yellow, m. 119-20.degree.). Et .alpha.-cyano-2-(2,3-dimethoxyphenyl)-3-ketocyclohexaneacetate (III), 90% (2,4-dinitrophenylhydrazone, yellow, m. 176-8.degree.). Me ester corresponding to I, an oil, 97% (2,4-dinitrophenylhydrazone, orange, m. 162-3.degree.); Me ester (IIIA) corresponding to III, m. 114.degree., 95% (2,4-dinitrophenylhydrazone, yellow, m. 167.degree.). Me .alpha.-cyano-3-keto-2-phenylcyclohexaneacetate, m. 86-7.degree. (2,4-dinitrophenylhydrazone, yellow, m. 155-7.degree.). 2-Phenyl-2-cyclohexen-1-one (0.1 mol.) and 0.2 mol. MeNO<sub>2</sub> with 0.025 mol. 30% Triton B methiodide in MeOH, kept 3 h. at 60.degree. and overnight at room temp., treated with 0.025 mol. AcOH, and dild. with 200 mL. ether, give 80% 3-nitromethyl-2-phenylcyclohexanone, m. 126.5-7.5.degree. (2,4-dinitrophenylhydrazone, yellow, m. 155-7.degree.); with MeONa the same yield of a slightly less pure product results; O<sub>2</sub>NCH<sub>2</sub>CO<sub>2</sub>Me (12 h. at 60.degree.) gives 90% crude Me 2-(2,3-dimethoxyphenyl)-3-keto-.alpha.-nitrocyclohexaneacetate, an oil. II (10 g.), 30 cc. anhyd. EtOH, 30 g. HC(OEt)<sub>3</sub>, and 0.1 g.

p-MeC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>Cl, refluxed 4 h., neutralized with MeONa, and the residue refluxed 4 h. with 20 mL. 50% aq. KOH, give 7.5 g. oily 3-keto-2-phenylcyclohexanemalonic acid (IV); Clemmensen-Martin redn. of 3.5 g. crude IV gives 2.8 g. trans-2-phenylcyclohexaneacetic acid (V), m. 110.degree.; 2 g. V in concd. H<sub>2</sub>SO<sub>4</sub>, heated 10 min. on the steam bath, gives 1.7 g. 1,2,3,4,4a,9,10,10a-octahydro-9-ketophenanthrene (VI), m. 95.degree.; oxime, m. 176.degree.; 2,4-dinitrophenylhydrazone, orange, m. 265.degree. (decompn.). Clemmensen-Martin redn. of 15 g. II, hydrolysis with aq. KOH, and decarboxylation at 180-200.degree. (10 min.) give 8 g. V. I (22.5 g.) on redn. yields 16.5 g. of a crude product which, refluxed 4 h. with 35 mL. 50% aq. KOH, gives 15 g. of a mixt. of malonic and acetic acids (VII), crystn. of which yields 6.6 g. 2-(2,3-dimethoxyphenyl)cyclohexanemalonic acid, m. 195-6.degree. (decompn.). The crude VII (13 g.) in 78 mL. AcOH and 52 mL. Ac<sub>2</sub>O, treated with 1.04 g. fused ZnCl<sub>2</sub>, refluxed 75 min., and dild. with 300 mL. H<sub>2</sub>O at a rate to maintain boiling, gives 65% 1,2,3,4,4a,9,10,10a-octahydro-9-keto-5,6-dimethoxyphenanthrene, m. 96-7.degree. [2,4-dinitrophenylhydrazone, crimson, m. 248.degree. (decompn.)] (this may be the product of Hornung, et al., C.A. 42, 1587h). II (10 g.) in 100 mL. 95% EtOH, hydrogenated (3 h.) over 0.5 g. Pt oxide at room temp. and 60 lb./sq. in., gives 9.8 g. Et 2-(2,3-dimethoxyphenyl)-3-hydroxycyclohexanemalonate (VIII) (acetate, m. 83-4.degree.); 10 g. VII and 30 mL. 50% aq. KOH, refluxed 1 h., give 6 g. of the acid (IX), m. 185.degree. (decompn.); 2 g. IX and 0.2 g. ZnCl<sub>2</sub> in 12 mL. AcOH and 10 mL. Ac<sub>2</sub>O, refluxed 1.75 h., give 0.7 g. of the acetate, m. 129.degree. [2,4-dinitrophenylhydrazone, crimson, m. 263.degree. (decompn.)], of 1,2,3,4,4a,9,10,10a-octahydro-4-hydroxy-9-keto-5,6-dimethoxyphenanthrene (0.32 g. from 0.5 g. acetate), m. 97.5-8.degree. [2,4-dinitrophenylhydrazone, crimson, m. 238-40.degree. (decompn.)]. I (10 g.), 30 g. HC(OEt)<sub>3</sub>, and 0.1 g. p-MeC<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>H in 30 cc. EtOH, followed by hydrolysis, give 2-(2,3-dimethoxyphenyl)-3-ketocyclohexanemalonic acid (X), with 0.5 mol. H<sub>2</sub>O, m. 98-100.degree. (decompn.); 15 g. X and 1.34 g. ZnCl<sub>2</sub> in 93 mL. AcOH and 65 mL. Ac<sub>2</sub>O, refluxed 75 min., the hot mixt. dild. with 400 mL. H<sub>2</sub>O, extd. with ether, washed with NaOH, evapd. to 30 mL. (3 g. of a compd. m. 105-10.degree. seps.), and the remaining oil refluxed 90 min. with 1.8 g. KOH in 30 mL. H<sub>2</sub>O, give 7 g. 1,2,3,4,4a,9,10,10a-octahydro-4,9-diketo-5,6-dimethoxyphenanthrene (XI), m. 115.degree. [dioxime, m. 210.degree. (decompn.)]; 10 g. X, decarboxylated (10 min.) at 200.degree. and the product treated with 50 g. HF, gives 90% XI. II (7 g.), 15 mL. (CH<sub>2</sub>OH)<sub>2</sub>, 30 mL. C<sub>6</sub>H<sub>6</sub>, and 0.1 g. p-MeC<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>H, refluxed 4 h. (H<sub>2</sub>O removed **azeotropically**), the oily residue refluxed 4 h. with 14 g. 50% aq. KOH, the product dild. with H<sub>2</sub>O, acidified to pH 8, extd. with ether, and the cooled ext. covered with 30 mL. C<sub>6</sub>H<sub>6</sub> and treated dropwise with an equiv. quantity of HCl, give 5.5 g. of the ethylene glycol ketal of 2-phenyl-3-ketocyclohexanemalonic acid (XII), m.

175-6.degree. (decompn.); XII, decarboxylated (10 min.) at 180-200.degree. and heated 10 min. on the steam bath with concd. H<sub>2</sub>SO<sub>4</sub>, gives 75% 1,2,3,4,4a,9,10,10a-octahydro-4,9-diketophenanthrene (XIII), m. 94-5.degree. [dioxime, m. 235.degree. (decompn.)]. Similarly, 6 g. of the ethylene glycol ketal (XIV), m. 182-3.degree., of IX yields 2 g. XI. IIIA yields 80% of the ethylene glycol ketal, m. 139-40.degree.; alk. hydrolysis gives 80% XIV. III (1 g.) in 5 mL. EtOH and 30 mL. 5% NaOH (24 h.) give some 2-(2,3-dimethoxyphenyl)-2-cyclohexen-1-one, m. 96.degree.. The ketal from 20 g. III in 150 mL. EtOH and 3.25 g. KOH in 40 mL. EtOH, kept 3 h. at room temp., give 15 g. .alpha.-cyano-2-(2,3-dimethoxyphenyl)-3-ketocyclohexaneacetic acid, m. 163-5.degree., decomp. 170.degree.; this could not be cyclized by AcOH-Ac<sub>2</sub>O-ZnCl<sub>2</sub> or by HF. Redn. of 20 g. III in 200 mL. EtOH over Pt oxide at room temp. and 60 lb./sq. in. gives 18.5 g. of the Et ester, an oil, of .alpha.-cyano-3-acetoxy-2-(2,3-dimethoxyphenyl)cyclohexaneacetic acid, m. 115.degree.; this could not be cyclized with AcOH-Ac<sub>2</sub>O-ZnCl<sub>2</sub> and the **ester** was not **cyclized** by HF. X, reduced (1 h.) over 5% Pd-C at room temp. and 60 lb./sq. in., gives a nearly quant. yield of 1,2,3,4,4a,9,10,10a-octahydro-4-keto-5,6-dimethoxyphenanthrene, m. 104-5.degree. [2,4-dinitrophenylhydrazone, orange, m. 183-4.degree.; oxime, m. 148-9.degree.; semicarbazone, m. 219-21.degree. (decompn.)]; the redn. can be carried out in AcOH at 60.degree.; partial Clemmensen redn. gives the same product. XIII (2 g.), reduced in AcOH over 10% Pd-C at 60-70.degree. and 60 lb./sq. in. (90 min.), gives 1.8 g. 1,2,3,4,4a,9,10,10a-octahydro-4-ketophenanthrene, m. 48-9.degree. (2,4-dinitrophenylhydrazone, yellow, m. 193-4.degree.; semicarbazone, m. 219.degree.). X yields the 4-(ethylene glycol) ketal, m. 134-5.degree., and XIII gives a similar deriv., m. 89.degree..

CC 10 (Organic Chemistry)

IT Homologous series

(**azeotrope** formation with members of)

IT 1,4-Dioxaspiro[4.5]**decane**-7-acetic acid,

.alpha.-cyano-6-(2,3-dimethoxyphenyl)-, methyl ester

1,4-Dioxaspiro[4.5]**decane**-7-malonic acid,

6-(2,3-dimethoxyphenyl)-

1,4-Dioxaspiro[4.5]**decane**-7-malonic acid, 6-phenyl-

4,9(1H,4aH)-Phenanthrenedione, 2,3,10,10a-tetrahydro-

4,9(1H,4aH)-Phenanthrenedione, 2,3,10,10a-tetrahydro-, cyclic ethylene acetal

4,9(1H,4aH)-Phenanthrenedione, 2,3,10,10a-tetrahydro-, dioxime

4,9(1H,4aH)-Phenanthrenedione, 2,3,10,10a-tetrahydro-5,6-dimethoxy-, cyclic ethylene acetal

4,9(1H,4aH)-Phenanthrenedione, 2,3,10,10a-tetrahydro-5,6-dimethoxy-, dioxime

9(1H)-Phenanthrone, 2,3,4,4a,10,10a-hexahydro-5,6-dimethoxy-

9(1H)-Phenanthrone, 2,3,4,4a,10,10a-hexahydro-5,6-dimethoxy-,  
 2,4-dinitrophenylhydrazone  
 Cyclohexaneacetic acid, 2-(2,3-dimethoxyphenyl)-.alpha.-nitro-3-oxo-  
 , methyl ester  
 Cyclohexaneacetic acid, .alpha.-cyano-2-(2,3-dimethoxyphenyl)-3-  
 hydroxy-, acetate  
 Cyclohexaneacetic acid, .alpha.-cyano-2-(2,3-dimethoxyphenyl)-3-  
 hydroxy-, acetate, Et ester  
 Cyclohexaneacetic acid, .alpha.-cyano-3-oxo-2-phenyl-, methyl ester  
 Cyclohexaneacetic acid, .alpha.-cyano-3-oxo-2-phenyl-, methyl ester,  
 2,4-dinitrophenylhydrazone  
 Cyclohexanemalonic acid, 2-(2,3-dimethoxyphenyl)-  
 Cyclohexanemalonic acid, 3-oxo-2-phenyl-, cyclic ethylene acetal  
 Cyclohexanemalonic acid, 3-oxo-2-phenyl-, diethyl ester  
 Cyclohexanemalonic acid, 3-oxo-2-phenyl-, diethyl ester,  
 2,4-dinitrophenylhydrazone  
 Cyclohexanone, 3-nitromethyl-2-phenyl-  
 Cyclohexanone, 3-nitromethyl-2-phenyl-, 2,4-dinitrophenylhydrazone  
 Spiro[1,3-dioxolane-2,4'(1'H)-phenanthren]-9'(4'aH)-one,  
 2',3',10',10'a-tetrahydro-  
 Spiro[1,3-dioxolane-2,4'(1'H)-phenanthren]-9'(4'aH)-one,  
 2',3',10',10'a-tetrahydro-5',6'-dimethoxy-

L35 ANSWER 18 OF 20 HCA COPYRIGHT 2005 ACS on STN

44:20020 Original Reference No. 44:3953f-i,3954a-h Synthesis of new homologs of hexestrol. Shishido, Keiichi; Nozaki, Hitoshi; Kuyama, Hiroshi (Kyoto Univ., Kyoto, Japan). Journal of Organic Chemistry, 14, 1124-9 (Unavailable) 1949. CODEN: JOCEAH. ISSN: 0022-3263.

AB The earlier method for the prepn. of hexestrol derivs. by dehalogenation condensation of p-(.alpha.-haloalkyl)anisoles (cf. S. and N., C.A. 42, 3371b) has been improved by using reduced Fe (I) in lieu of Fe powder, making the method generally applicable. Anethole (40 g.) in 200 cc. PhMe cooled with ice-NaCl is satd. with anhyd. HBr, the PhMe soln., washed with ice-H<sub>2</sub>O, added over a period of 15 min. to 24 g. I in 240 cc. H<sub>2</sub>O at 80-98.degree. (the PhMe being **distd.** off with the water during the addn.), the mixt. refluxed 3 hrs. at 95-8.degree., cooled, extd. with ether, and the washed and dried ether soln. evapd., giving 20% meso-3,4-bis(p-methoxyphenyl)hexane (II), plates from MeOH-ligroin, m. 144.degree.. **Distn.** of the residue of the mother liquor gives 9 g., b<sub>23</sub> 70-115.degree., and 17 g., b<sub>6</sub> 180-200.degree.. The latter fraction seems to contain dl-(MeOC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>Et)<sub>2</sub> and possibly an anethole dimer. With the Cl analog the yield of II is only 14-15%. Reducing 10 g. 2,4-Me(CH<sub>2</sub>:CH)C<sub>6</sub>H<sub>3</sub>OMe in 50 cc. ligroin, satd. with HCl at -8 to -10.degree., with 5 g. I in 60 cc. H<sub>2</sub>O 4 hrs. at 100.degree. gives 6 g. of a fraction, b<sub>6</sub> 180-93.degree., from which is isolated 1.5 g. meso-2,3-bis(4-methoxy-m-tolyl)butane (III), m. 124-5.degree.. III, demethylated with a Grignard reagent or HI in AcOH, gives the p-HO

analog, large crystals soon changing to a white powder, m. 174-5.degree. (di-Ac deriv., prepd. with Ac<sub>2</sub>O + C<sub>5</sub>H<sub>5</sub>N, m. 145-5.5.degree.). Isosafrole (IV) (50 g.) in 100 cc. ligroin is satd. with HBr, treated with 20 g. I in 200 cc. H<sub>2</sub>O at 100.degree., and the mixt. extd. with C<sub>6</sub>H<sub>6</sub>, giving 12 g. crystals (V). The residue of the evapd. mother liquor is **distd.**, giving 3 fractions, (a) 1 g. contg. 43% IV, b35-40 60-100.degree., (b) 9 g. contg. 91.2% IV, b35-40 120-30.degree., and (c) 13 g., b3 210.degree., from which is isolated 4 g. V. Recrystn. of V gives 12 g. meso-3,4-bis-(3,4-methylenedioxyphenyl)hexane (VI), m. 174-5.degree.. Refluxing 10 g. VI 3 hrs. in 45 g. PhMe with 42 g. PCl<sub>5</sub> and decomp. the 3,4-bis(3,4-dichloromethylenedioxyphenyl)hexane with ice and satd. Na<sub>2</sub>CO<sub>3</sub> soln. give 3,4-bis(3,4-carbonyldioxyphenyl)hexane (VII), m. 186-7.degree.. Heating 6 g. VII, 320 g. MeOH, and 100 cc. concd. HCl 2.5 hrs. in a CO<sub>2</sub> atm. at 78.degree. and **distg.** off 2/3 of the solvent give 5 g. 3,4-bis(3,4-dihydroxyphenyl)hexane, m. 230-5.degree. (decompn.) (cf. Baker, C.A. 37, 5714.4) (tetra-Ac deriv., m. 167-7.5.degree., also obtained on direct acetylation of VI with Ac<sub>2</sub>O at 200.degree. for 15 hrs.). To obtain the best conditions for the dehalogenation condensation 100 g. IV in 150 cc. PhMe, satd. with HBr at -10.degree., is reduced with 40 g. I in 400 cc. H<sub>2</sub>O by 3 different methods: (A) at 100.degree. with slow addn. of the HBr soln. at such a rate that the PhMe is completely **distd.** off, giving 35 g. of fraction a, 45 g. b, and 20 g. c; (B) the HBr soln. is dropped into the I-H<sub>2</sub>O mixt. at 80-90.degree., giving 33 g. a, 53 g. b, and 25 g. c; (C) the HBr soln., I, and H<sub>2</sub>O are mixed at room temp. and gradually heated and the PhMe **azeotropically distd.** off, giving 25 g. a, 50 g. b, and 23 g. c. Refluxing 30 g. safrole-HBr, b8 130-40.degree., and 15 g. I with 150 cc. H<sub>2</sub>O 2 hrs. with stirring gives only a very small amt. of a condensation product. Reduction of 10 g. o-methylanethole in 60 cc. PhMe or ligroin satd. with HBr with I in 60 cc. H<sub>2</sub>O gives 3 g. condensation product from which, on repeated crystn. from MeOH, is isolated 0.6 g. meso-3,4-bis(4-methoxy-o-tolyl)hexane, large prisms, m. 120-30.degree.; demethylated with HI in AcOH, it gives the p-HO analog, m. 218-19.degree. (di-Ac deriv., needles, m. 153.degree.). p-MeOC<sub>6</sub>H<sub>4</sub>CH:CH<sub>2</sub>Et (10 g.) treated with HBr and reduced with I in H<sub>2</sub>O gives 3.5 g. condensate from which is isolated 1 g. meso-4,5-bis(p-methoxyphenyl)octane (VIII), m. 121-2.degree., demethylated to the p-HO analog (octestrol), m. 166-7.degree. (di-Ac deriv., m. 167.5-8.5.degree.). In the same way, 13 g. p-MeOC<sub>6</sub>H<sub>4</sub>CH:CMe<sub>2</sub> gives 3 g. of an oily mixt. of meso- and dl-2,7-dimethyl-4,5-bis(p-methoxyphenyl)octane which is directly demethylated, giving 0.5 g. p-HO analog, long needles soon changing to a powder, m. 167-70.degree. (di-Ac deriv., m. 187-90.degree.). Reduction of p-MeOC<sub>6</sub>H<sub>4</sub>CHBrBu from 12 g. olefin gives 1 g. 5,6-bis(p-methoxyphenyl)**decane**, demethylated to



meso-5,6-bis(p-hydroxyphenyl)**decane** (decestrol), long needles, m. 170-1.degree. (di-Ac deriv., m. 128.5-9.degree.). p-MeOC<sub>6</sub>H<sub>4</sub>CH:CHBu (20 g.), treated with HBr, reduced, and demethylated, gives 2 g. 6,7-bis(p-hydroxyphenyl)**dodecane**, hair-like crystals from C<sub>6</sub>H<sub>6</sub>, m. 145-6.degree. (di-Ac deriv., fibrous brilliant crystals, m. 98-9.degree.). p-MeOC<sub>6</sub>H<sub>4</sub>COC<sub>17</sub>H<sub>35</sub>, m. 78-9.degree., is reduced to the carbinol and the latter is dehydrated, giving p-MeOC<sub>6</sub>H<sub>4</sub>CH:CHC<sub>16</sub>H<sub>33</sub> (IX), b<sub>0.015</sub> 170-80.degree.. Treating IX in PhMe with HBr and reducing the mixt. with I failed to give any **distillable** condensation product. Refluxing 25 g. PhCHBrCH<sub>2</sub>Br (X) with 5.6 g. I in 64 cc. H<sub>2</sub>O 8 hrs. and **distg.** the reaction product give 2 fractions, (d) 2.5 g., b<sub>20-30</sub> 50-7.degree., and (e) 2.7 g., b<sub>5</sub> 110-20.degree.. Bromination of d gives X; e is assumed to be a dimer of styrene.

CC 10 (Organic Chemistry)

IT Anisole, p-1-octadecenyl-

Bibenzyl, 3,4,3',4'-bis(dichloromethylenedioxy)-.alpha.,.alpha.'-diethyl-

Bibenzyl, 4,4'-dimethoxy-.alpha.,.alpha.',3,3'-tetramethyl-, meso-

Bibenzyl, 4,4'-dimethoxy-.alpha.,.alpha.'-dipropyl-, meso-

Bibenzyl, .alpha.,.alpha.'-dibutyl-, 4,4'-dimethoxy-

Bibenzyl, .alpha.,.alpha.'-diethyl-4,4'-dimethoxy-2,2'-dimethyl-, meso-

Bibenzyl, .alpha.,.alpha.'-diisobutyl-4,4'-dimethoxy-, dl-

Bibenzyl, .alpha.,.alpha.'-diisobutyl-4,4'-dimethoxy-, meso-

Carbonic acid, **ester (cyclic)**, with

4,4'-(1,2-diethylethylene)dipyrocatechol

Phenol, 4,4'-(1,2-dibutylethylene)di-, diacetate

Phenol, 4,4'-(1,2-dibutylethylene)di-, meso-

Phenol, 4,4'-(1,2-diisobutylethylene)di-, diacetate

Phenol, 4,4'-(1,2-diisobutylethylene)di-, dl-

Phenol, 4,4'-(1,2-diisobutylethylene)di-, meso-

Phenol, 4,4'-(1,2-dipentylethylene)di-, diacetate

Phenol, 4,4'-(1,2-dipropylethylene)di-, meso-

Phenol, 4,4'-(1,2-dipropylethylene)di-, meso-, diacetate

m-Cresol, 4,4'-(1,2-diethylethylene)di-, diacetate

m-Cresol, 4,4'-(1,2-diethylethylene)di-, meso-

o-Cresol, 4,4'-(1,2-dimethylethylene)di-, diacetate

o-Cresol, 4,4'-(1,2-dimethylethylene)di-, meso-

L35 ANSWER 19 OF 20 HCA COPYRIGHT 2005 ACS on STN

36:18589 Original Reference No. 36:2838g-i,2839a-i,2840a-b Catalytic hydrogenation with recording of temperature and pressure. II.

Application to the benzene nucleus. Palfray, L. Bull. soc. chim., 7, 407-30 (Unavailable) 1940. OTHER SOURCES: CASREACT 36:18589.

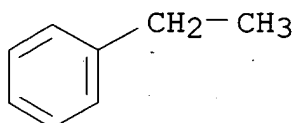
AB Com. thiophene-free benzene was hydrogenated while raising the temp. every 15 min., the yield being 97.5% of very pure cyclohexane. The relative speeds of absorption of H were plotted, showing absorption

to be 40 times as rapid at 155.degree. as at 40.degree.. In 1 case some absorption took place at 15.degree.. Toluene was hydrogenated under similar conditions (115 kg. pressure). H was absorbed slightly at 70.degree. and in quantity at 150.degree., giving practically pure methylcyclohexane in 5 h. A Me group thus hindered hydrogenation. In the case of o-, m- and p-xylene, absorption started at 65-70.degree. and increased at 125.degree. for the p-isomer, and 210.degree. for the other 2, the reaction being complete in 2 h. In the case of naphthalene, H was absorbed first at 100.degree. and rapidly at 125.degree.. Tetrahydronaphthalene was produced in 30 min. The 2nd absorption started at 175.degree. and became rapid at 200.degree., giving decalin. Control of the temp. and the difference in b. ps. permitted easy sepn. of these 2 products. One mol. of benzyl alc. was hydrogenated with 2 g. Raney Ni, the reaction starting at 90.degree. and continuing at 100.degree. for 2 h. The products of distn. were water and toluene (sepd. by decantation), an azeotropic mixt. of toluene (50%), benzyl alc. and hexahydrobenzyl alc. (20%) and unreacted alc. PhCH<sub>2</sub>CH<sub>2</sub>OH (200 g.) absorbed H rapidly at 235.degree., giving 3 distn. products, the 1st (50 g.) b. 77-85.degree., the 2nd (24 g.), b. 125-45.degree., contg. EtPh and the 3rd, b. 190-3.degree., contg. 2-(hexahydrophenyl)ethanol. This product could be obtained in better yield if the reaction was carried out at a higher temp. for a shorter time. BzH absorbed 3 mols. H when heated to 105.degree.. When the reaction was kept at 60.degree., the H pressure fell 20 kg. in 16 min., the reaction taking a total of 20 min. The products were benzyl alc. and a small amt. of BzOH, probably contained in the original aldehyde. Higher temps. were necessary for the deoxidn. Anisaldehyde (565 g.) was hydrogenated for 2 h. with 4 g. Raney Ni, absorption starting at 30.degree. and becoming rapid at 90.degree.. The product was 97% of anisyl alc. .alpha.-Amylcinnamaldehyde was hydrogenated for 1 h., absorption starting at 30.degree. and becoming rapid at 60-5.degree.. The reaction yielded 90% of .alpha.-amyhydrocinnamaldehyde. Hydrogenation at 150.degree. gave 75% of .alpha.-amyhydrocinnamaldehyde and at 220-30.degree. gave principally 3-cyclohexyl-2-pentyl-1-propanol. Coumarin (1.3 g.) under 150 kg. pressure began absorbing H at 40.degree., and did so rapidly at 80.degree.. After an hr. pure hydrocoumarin was obtained. Coumarin was also hydrogenated successfully at 125-30.degree. and pressures never exceeding 30 kg. The double bond in the .alpha.-position to the lactone group was completely satd. in 2 h. Acetophenone (1300 g.) was hydrogenated (5 g. Ni), absorption taking place at 30-5.degree., at which point the temp. rose to 45-50.degree., and the H pressure fell 15 kg. in 12 min. The temp. was raised to 60.degree. and kept there and the pressure fell 10 kg. in 12 min. The H pressure was allowed to fall to 0 kg., was raised to 145 kg., allowed to fall again and the

process continued until no more H was absorbed. The yield of PhCH(OH)Me was practically quant., apparently no dehydration taking place. Under similar conditions with p-methylacetophenone absorption became quite rapid at 50.degree. (30-kg. fall in pressure in 33 min.) and increased at 80.degree. (30-kg. fall in 18 min.). 1-C<sub>10</sub>H<sub>7</sub>COMe (contg. some 2-isomer) began absorbing at 80.degree. and absorbed rapidly at 105-10.degree.. Two fractions were obtained, the first b<sub>17</sub> 163-4.degree., corresponding to 87% of (tetrahydro-1-naphthyl)methylcarbinol and 15% of the corresponding ketone, and the 2nd, b<sub>18</sub> 170-2.degree., corresponding to 96% of 1-naphthylmethylcarbinol and 2.7% of the corresponding ketone. Hydrogenation of 2-C<sub>10</sub>H<sub>7</sub>COMe at 60.degree. gave after 5 h. 60% of what was probably the carbinol and 6% of unchanged ketone; at 85.degree. it gave what was probably a mixt. of the corresponding tetrahydro derivs. From the hydrogenation of .alpha.- and .beta.-ionone, it was concluded that at 65.degree. the extracyclic ethylenic double bond was satd., at 90.degree. the ketone function was reduced, at 240.degree. the cyclic residue was satd., and at 270.degree. dehydration took place. Phenol (2 mols.) was hydrogenated at 120 kg. (4 g. Ni); at 42.degree. absorption began, and at 65.degree. it became rapid. The reaction mixt. was held at 95.degree., at which temp. the pressure dropped 60 kg. in 12 min. The reaction was continued 40 min. and gave 97% of cyclohexanol. When, on the other hand, the reaction mixt. was rapidly heated to 90.degree., the H pressure dropped 85 kg. in 6 min.; on further heating to 250.degree., an endothermic reaction took place, giving at 285.degree. 130 g. (from 2 mols.) cyclohexane. o-, m- and p-Cresol were similarly hydrogenated at 95.degree.. The o-deriv. required 90 min., the m-compd. 244 min. and the p-isomer 160 min. The yields were, resp., 90% 2-methylcyclohexanol, 68% of the 3-Me isomer and 81% of the 4-Me isomer. Some dehydration took place. Pyrocatechol, resorcinol, and hydroquinone were similarly treated in the absence of solvents. Rapid absorption took place at 145.degree. for the o-, 130.degree. for the m-, and 125.degree. for the p-deriv., and was completed in 2 h. at 150.degree., giving quant. yields of the cyclohexanediols. Hydroquinone was hydrogenated at 145.degree. (rapid absorption at 100-5.degree.), giving a quant. yield of 1,4-cyclohexanediol in an hr. 1,4-Dimethyl-2-hydroxybenzene was hydrogenated at 94.degree. in 8 h. It showed the properties which would be expected from o-cresol counterbalanced by m-substitution. In the case of 1,2-dimethyl-4-hydroxybenzene, absorption began at 85.degree. and was found to proceed rapidly at 120.degree.. In this case the properties were those of m-cresol augmented by p-substitution. Thymol (400 g.) was hydrogenated with 4 g. Ni at 150 kg., absorption beginning at 100.degree.. The temp. was held at 120-5.degree. and the reaction was complete in 10 h., the product being 95% of menthol. Carvacrol similarly treated began absorbing at 125.degree.; the temp. was held at 150-5.degree. and

the reaction was complete in 6 h., yielding 96% carvomenthol. Four H atoms were successfully and rapidly added to 1- and 2-naphthol, the temp. being kept below 90.degree.. At 120-35.degree. the naphthols yielded decahydronaphthols. 14 pressure-temp. curves are given.

IT 100-41-4, Benzene, ethyl-  
 (formation of, from phenethyl alc. hydrogenation)  
 RN 100-41-4 HCA  
 CN Benzene, ethyl- (7CI, 8CI, 9CI) (CA INDEX NAME)



CC 10 (Organic Chemistry)  
 IT 100-41-4, Benzene, ethyl-  
 (formation of, from phenethyl alc. hydrogenation)

L35 ANSWER 20 OF 20 HCA COPYRIGHT 2005 ACS on STN

32:64632 Original Reference No. 32:9051b-i -Ether-like compounds. I. Preparation of acetals and ketals. Salmi, Einar J. Ber., 71B, 1803-8 (Unavailable) 1938.

GI For diagram(s), see printed CA Issue.

AB Boeseken and Tellegen (C. A. 32, 3335.9) report they have been unable to obtain certain cyclic acetals (e. g., those of cyclopentanone and of AcCH<sub>2</sub>CO<sub>2</sub>Et) with the P<sub>2</sub>O<sub>5</sub> method of Smith and Lindberg (C. A. 25, 3629). S. has readily obtained these acetals by another method. The water formed in the condensation reaction, which hinders further ketalization, can often best be removed by **azeotropic distn.** The reason this method has been used so seldom in the prepn. of esters, ethers and acetals has probably been the lack of simple and easily constructed app. The simplest is that of Meyer (C. A. 18, 54) for the prepn. of aromatic sulfonic acids. The advantages of the method in the prepn. of acetals are: the acetal formation can be carried almost to completion; calcd. amts. of the reactants are sufficient; only a small amt. of catalyst is required; the product remaining in the **distg.** bulb is water-free and readily worked up. In some cases, however, the method is less satisfactory or not at all applicable, as, e. g., when the aldehyde or alc. boils so low that it forms the main part of the **distillate** or when the b. ps. of the acetal and the solvent are so close together that sepn. of the 2 substances is difficult. The prepn. of the following cyclic ketals is described (the values given are for d<sub>420</sub> and n for .alpha., D and .beta., resp., at 20.degree.). Et acetoacetate: ethylene (35 g. from 30 g. AcCH<sub>2</sub>CO<sub>2</sub>Et, 16 g. (CH<sub>2</sub>OH)<sub>2</sub> and a few